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AFRPL-TR-72-60

AMBIENT TEMPERATURE CURE CATALYSTS FOR CARBOXY BINDER SYSTEMS

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Allegany Ballistics Laboratory
Hercules, Inc.

TECHNICAL REPORT AFRPL-TR-72-60

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Air Force Rocket Propulsion Laboratory
Air Force Systems Command
Edwards Air Force Base, California 93523

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FOREWORD

This technical report relates work performed under Contract F04611-70-C-0018, Air Force Rocket Propulsion Laboratory, Edwards, California 93523, for the development of ambient cure catalyst systems for solid propellants based on carboxyl containing binders. The catalyst screening and chemistry studies were performed in the Physical Sciences Division of Midwest Research Institute, Kansas City, Missouri, and the propellant processing and evaluation studies were conducted by Hercules, Inc., Allegany Ballistics Laboratory, Cumberland, Maryland. The Air Force Project Engineer was Captain D. F. Clark, USAF, AFRPL.

Personnel at MRI contributing to the program were: Dr. A. D. McElroy, Program Supervisor from January 1970 to November 1972; Dr. R. E. Foscante, Project Leader and Program Supervisor for the final period of the program; Mrs. C. Weis, Assistant Chemist; and Mr. C. J. Wiegand, Senior Chemist. Those contributing at ABL were: Mr. H. Gilbert, Program Supervisor; Dr. T. Comfort, Project Leader; and Mr. C. Dickey.

The inclusive dates of the program technical effort were January 1970 to March 1972. No classified material is contained in the report nor was any classified information abstracted from classified sources.

Publication of this report does not constitute Air Force approval of the findings and/or conclusions stated herein. It is published only for the exchange and stimulation of ideas.

This technical report has been reviewed and is approved for distribution.

CHARLES R. COOKE
CHIEF, SOLID ROCKET DIVISION

ii

ABSTRACT

An extensive series of organometallic compounds were screened to determine their utility as catalysts for the ambient temperature cure of carboxylic acid terminated polymers with epoxide and aziridine curatives. Chromium salts, specifically chromium 2-ethyl hexanoate, were shown to promote the desired cure reaction efficiently and stoichiometrically at 1% and less levels at 25°C in less than 7 days in both model and binder cure studies. The presence of other propellant components (e.g., ammonium perchlorate, aluminum, iron oxide, antioxidants, surfactants, plasticizers, etc.) and certain contaminants (water, perchloric acid) showed no significant or uncontrollable effects on the course of the Cr catalyzed reaction of both model and binder systems. Catalytic trends appear similar in both aziridine and epoxide systems. Reaction mechanisms and catalyst design parameters were developed and are discussed.

Using the catalyst system selected by Midwest Research Institute, composite propellants based on several different carboxy binder systems were successfully manufactured and cured at ambient temperature (75°F) by ABL. A 6-month surveillance program proved that chromium-octoate-catalyzed propellants had completely cured at ambient and did age as well as 140°F-cured control propellants. The Telagen-epoxide ambient-cured binder system, which was the prime candidate in this program, is deemed ready for scale-up beyond the 40-lb. batch size, 85.5% total solids propellant demonstrated in this program.

TABLE OF CONTENTS

TABLE OF CONTENTS (Concluded)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Continued)

LIST OF ILLUSTRATIONS (Continued)

LIST OF ILLUSTRATIONS (Concluded)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF TABLES (Concluded)

I.

INTRODUCTION

A. Background

Some of the well known advantages of the solid propellant are: simplicity of design, instant availability (compared to cryogenics), and high density. In simplest terms, the composite solid propellant consists of a polymeric matrix containing the other ingredients (oxidizer, fuel) which participate in the combustion process. The curing of the propellant is actually an in situ polymerization process, the results of which control the mechanical, physical, and often combustion properties of the final propellant.

Stresses and strains which may lead to the formation of cracks in the propellant must be avoided. High strains in the port area may result from shrinkage due to a decrease in polymer volume on cure and temperature drop upon cool-down of the motor from the 130° to 160°F cure temperature. The shrinkage due to cool-down may be avoided by using a catalyst to drive the cure reaction at a reasonable rate at ambient (70°F) temperature.

Ambient cure also gives the propellant a comparatively low stress-free temperature (80°F vs. the usual 160°F). The advantage of an 80°F stress-free temperature is lower thermal strains upon exposure of the motor to cold temperatures and only mild compressive forces on the grain at high temperatures.

The general types of binder systems of interest on this program are the carboxylic acid terminated prepolymers cured with either epoxides or aziridines. Currently, elevated temperatures are required to effect the cure of propellants based on these binders.

The interactions which can affect the mechanical and physical properties and aging characteristics of a propellant can be summarized as follows:

1. Homopolymerization or rearrangement of curatives (especially significant for the aziridines).

2. Side reaction of the curative during cure with other ingredients, notably the oxidizer.

3. Postcure reactions due either to side products generated in 2, or to slow reaction of functionalities of the cured propellant with other components (leading to hardening of the propellant).

1

4. Chemical or thermal instability of the cure linkage leading to cure reversal (softening of the propellant).

5. Cracking of the propellant during cool-down from cure due to the large difference in the coefficient of thermal expansion between the case and the propellant.

Many of these problems can be either eliminated or mitigated by catalyzing the cure reaction. Reaction rates can be accelerated at lower (or ambient) temperatures, thereby eliminating the cool-down and its attendant differential volume change. The main cure reaction can be promoted in the correct direction at the expense of side reactions and homopolymerization. Those postcure reactions proceeding from side products would then be controlled. Of course, another benefit would arise from the cost savings involved in curing propellants at ambient temperature.

Some problems may arise, however, in utilizing an ambient cure process. The lower the temperature, the greater is the slurry viscosity of the formulation. In certain systems ambient mixing and casting may be difficult (especially those of high solids loading). If the temperature is raised to increase fluidity, the presence of a rate accelerator in the mix will cause pot life problems.

Cure reversal is another potential problem in a catalyzed system. There are instances in which a catalyst will assist in cleavage of the bond it helped form (e.g., as may occur in the urethane system). In addition, the cure catalyst may promote side reactions between other functionalities in the propellant during storage (e.g., oxidative cross-linking of double bonds).

To recapitulate, the probable benefits of an ambient temperature propellant cure catalyst system are several, including the following: reduction in the liklihood of undesirable physical and chemical phenomena during cure; increased control of the specificity of cure chemistry, and therefore, of the properties of the cured propellant; a lower stress-free temperature, increase in the variety of binder systems amenable to cure; reduction in the complexity and cost of formulation and cure; and a better opportunity to successfully handle advanced propellant ingredients.

B. Objectives

The overall objective of this program is the development and demonstration of ambient temperature cure catalyst systems for propellants containing the carboxylic acid-epoxide and aziridine based binder. The specific approach to the problem involves the following steps.

2

1. A survey of the literature, to define the state of the art in this area and identify useful information from related fields.

2. Select a series of candidate catalysts giving desirable reaction rate and stoichiometry.

3. Evaluate those candidates in the presence of propellant components and potential contaminants.

4. Develop and demonstrate processing procedures to utilize the ambient temperature cure catalyst.

5. Evaluate the aging characteristics of solid propellants formulated with these cure catalyst systems.

C. Approach

The literature survey indicated the types of materials most likely to be effective as catalysts for the epoxide-carboxylic acid condensation reaction. The selection procedure involves screening the potential catalysts in a model reaction system to obtain relative rate and reaction direction data. The model system approach was taken because it provides a rapid and simplified method for evaluating large numbers of materials. In addition, these reaction studies can be designed so that the effects of selected reaction parameters on rate and stoichiometry can be evaluated. 2-Ethyl hexanoic acid (EHA) and allyl glycidyl ether (AGE) were selected as model reactants; gas-liquid chromatography was employed to monitor the rate and stoichiometry of consumption of reactants and the formation of products. In addition, selected propellant components and contaminants were introduced into the model system and their effects on reaction rate and stoichiometry were determined.

Those materials surviving the screening studies were then evaluated as cure catalysts in the actual binder system in two types of studies: (1) reaction chemistry through the use of an infrared method to follow the course of the cure reaction; and (2) gumstock and low solids-loaded binder studies as a prelude to processing evaluation using conventional physical property measurements. The effects of propellant ingredients and contaminants on the rate and direction of the catalyzed cure reaction are also under study in these binder studies.

Ambient temperature processing procedures are evaluated and developed in terms of processability and cure characteristics in a series of propellant mix studies ranging from 30 g. to 30 lb. Finally, the aging characteristics of propellants cured with the candidate catalysts (and in some cases with contaminants present) are evaluated in both model and propellant surveillance studies.

CATALYST SCREENING (EPOXIDE SYSTEM)

A. Selection of Catalysts for Initial Screening

The characteristics of a good cure catalyst are apparent from previous discussion. Notably, such a material must: (1) catalyze only the main reaction; (2) be stable in the propellant environment; (3) be effective in low concentration; (4) control the reaction at a rate conducive to good pot life; (5) be highly soluble in the binder; (6) be intrinsically stable (it must not itself decompose); (7) not contribute to reversal of the cure reaction; (8) be nonreactive with components of the formulation; and (9) require no special handling.

The literature indicates that a wide number of materials (of the mineral and Lewis acid type) have been used to accelerate the opening of the epoxide ring and facilitate condensation of the epoxide with nucleophilic species. The major similarity of these catalytic materials is the fact that they are electrophilic in nature, that is, they are capable of attracting electron rich atoms or groups to themselves. Many of these materials are not suitable for use in propellants because they may catalyze the wrong type of reaction (e.g., epoxide homopolymerization instead of carboxylic acid-epoxide addition esterification) or they may be ineffective or incompatible in the propellant environment. Catalysis by organometallics takes precedence in propellant chemistry as a means of catalyzing the cure reaction because of the apparent efficiency, and ease of handling, storage, and use of these catalysts.

B. Reaction Paths and Experimental Design

Possible reaction paths for the carboxylic acid-epoxide reaction include:

$$\text{Path A: } M \longrightarrow \text{homopolymerization}$$

$$\sim CH_2-CH_2-O-CH_2-CH_2 \sim$$

Epoxide starting material:

$$\underset{R'}{HC}\overset{O}{\diagdown\diagup}\underset{R''}{CH}$$

Path B ($-\overset{O}{\overset{\|}{C}}-OH$):

$$-\overset{O}{\overset{\|}{C}}-O-\underset{R}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-R$$

Long time or elevated temperatures required.

Path C ($-\overset{O}{\overset{\|}{C}}-OH$ / M):

$$-\overset{O}{\overset{\|}{C}}-O-\underset{R'}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-R'' \quad \text{(attack at) } \text{C-R'} \quad \text{(C-1)}$$

When R' = R", C-1 = C-2
Where R' ≠ R" substitution occurs preferentially on the least substituted carbon.

$$+$$

$$-\overset{O}{\overset{\|}{C}}-O-\underset{R''}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-R' \quad \text{(attack at) } \text{C-R''} \quad \text{(C-2)}$$

Path D ($-\overset{O}{\overset{\|}{C}}-OH$ / M):

$$-\overset{O}{\overset{\|}{C}}-O-\underset{R'}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{O-\overset{O}{\overset{\|}{C}}\sim}{\underset{|}{\overset{|}{C}}}}-R''$$
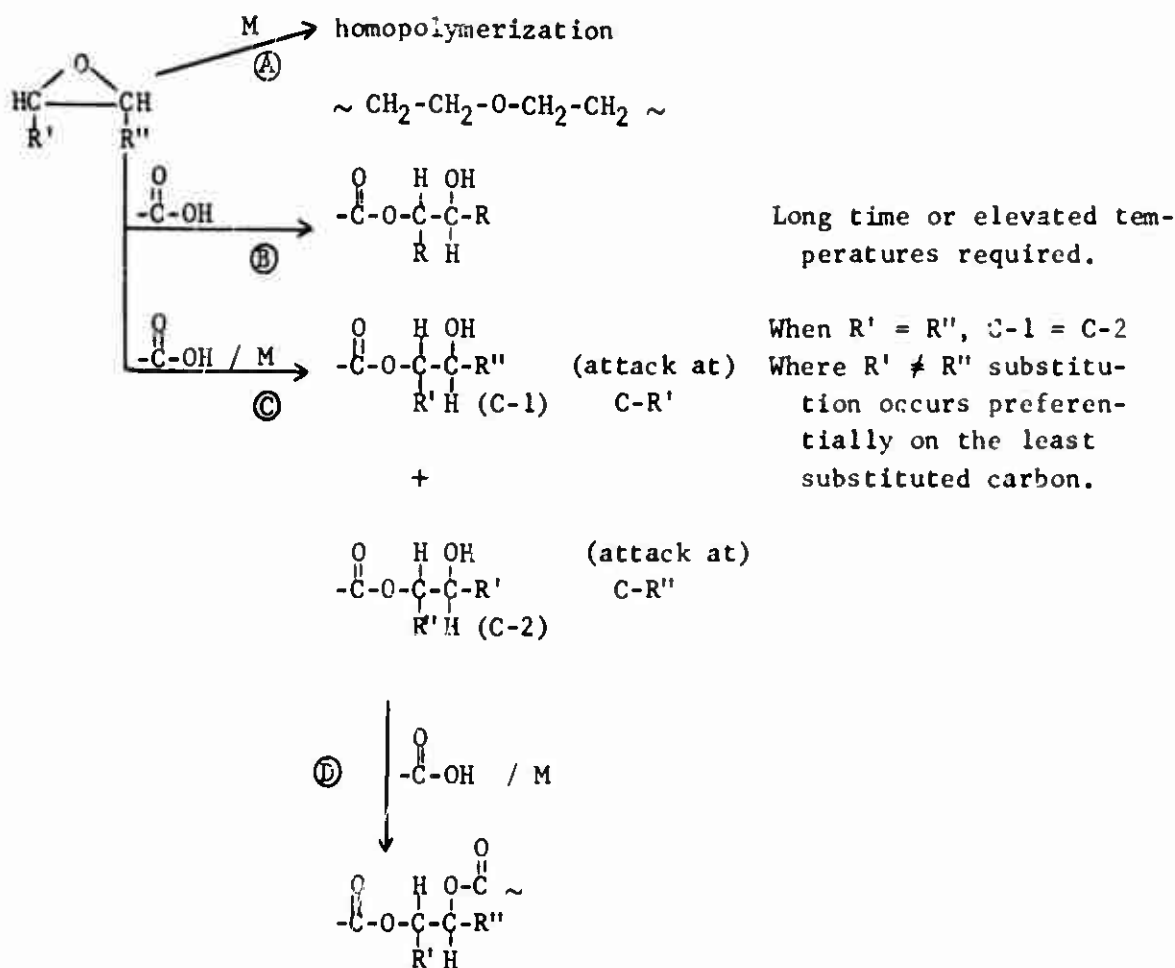
Reaction Path A is a possibility only in the catalyzed systems under the low temperature conditions of this study. (The epoxides used are stable at ambient and test temperatures.) Reaction B is an extremely slow reaction, and is mentioned here for the sake of completeness (for the screening studies, stock solutions of acid and epoxide are prepared in advance of most determinations; hence, their reactivity, if any, during storage must be known). Path C is the main and desired reaction route, that is, to compound C (where R' - R", C-1 and C-2 are identical). For unsymmetrical epoxides (as are found in the curatives) addition of the carboxyl group will occur on the least substituted carbon (Ref. 1). When R' = H and R" = alkyl, C-1 will be the favored product; that is, the main reaction product will be a β-hydroxy ester with the hydroxyl group in a secondary configuration on the main carbon chain (in the binder the hydroxyl group will be in a secondary position along the polymer backbone). The unfavored product would contain the alcohol group as a primary substituent on a side chain (C-2 where R' = H, R" = alkyl group). Path D represents a route which could conceivably be a competitive reaction to Route C during the cure reaction (depending on the catalyst present) and also be a postcure reaction

5

situation through condensation of unreacted carboxylic acid starting material with the hydroxyl group of the product ester.

Hence, the ideal catalyst will be either specific to the acid-epoxide condensation or will direct the reaction through Route C to product C-1 (where R' ≠ R'' and R' = H) sufficiently fast so that Path D is eliminated because the least reactive product (secondary alcohol along the polymer backbone should be more sterically hindered than the primary hydroxyl of the unfavored ester and hence, less reactive, if, indeed, such a condensation were to occur) is formed and acid is consumed preferentially in Path C.

In light of this discussion, the data required from the catalyst screening experiments are as follows: (1) relative rates of disappearance of acid and epoxide and the stoichiometry of the consumption; (2) extent to which a given catalyst will cause homopolymerization of the epoxide; (3) the number, relative abundance, and identity of products formed; and (4) the extent to which reaction of starting acid and product hydroxy ester is possible. The above data items can be derived directly from the gas chromatographic screening runs (except for the identity of the products); Items 2 and 4 are the subject of additional corroborative studies.

C. Catalyst Screening Studies

The effects of metal type, ligand nature, and temperature on the rate and stoichiometry of the acid-epoxide reaction were studied in an experimental series utilizing 2-ethyl hexanoic acid (EHA) and allyl glycidyl ether (AGE) as models. Table I lists the materials evaluated in this series. The results of these screening experiments have suggested three categories of catalytic effectiveness for the acceleration of the epoxide-acid reaction. The chromium salts give complete reaction in less than 2 days at 50°C and less than 7 days at 25°C. Iron salts, specifically, ferric octoate, were shown to accelerate the AGE-EHA reaction at a rate less than the analogous chromium salts, but still at a rate which is faster than most other materials and within the desired performance range. The value of the intermediate performing catalysts was assessed as follows: (1) should the chromium salts have proven to be too fast for good pot life behavior, a slower catalyst would be required; (2) should cure reversal during aging be indicated, the intermediate group would prove a mild compromise rate accelerator.

6

TABLE I

SUMMARY OF CATALYST SCREENING STUDIES

Catalyst	Catalyst Level (wt. %)	Temperature (°C)	% Reaction[a]		
			7 Days	14 Days	30 Days
CrOct	1	25	99	100	100
	1	50	100	100	100
CrOleate	1	25	95	100	100
	1	50	100	100	100
CrNapthenate	1	25	95	100	100
	1	50	100	100	100
Cr-neo-decanoate	1	25	97	100	100
	1	50	100	100	100
$Cr(AA)_3$	1	25	< 1.0	-	.?
	1	50	5.5	10.7	72.2
MnOct	2	25	-	2.5	25.2
	2	50	8.3	22.2	58.3
CoOct	1	25	11.3	-	25.9
	1	50	23.6	-	48.7
NiOct	1	25	7.8	-	8.8
	1	50	19.8	-	20.1
ZrOct	1	25	< 1.0	-	< 1.0
	1	50	6.8	-	10.0
$Zr(AA)_3$	1	25	< 1.0	..	3.5
	1	50	7.2	-	15.2
CuOct	1	25	< 1.0	-	5.8
	1	50	< 1.0	-	38.2
$Co(AA)_2$	1	25	12.0	-	48.0
	1	50	27.7	52.7	83.8
$Co(AA)_3$	1	25	< 1.0	-	-
	1	50	11.0	-	23.5

TABLE I (Continued)

Catalyst	Catalyst Level (wt. %)	Temperature (°C)	% Reaction[a]		
			7 Days	14 Days	30 Days
$Fe(AA)_2$	1	25	< 1.0	-	44.4
	1	50	25.0	55.5	77.8
$Fe(AA)_3$	1	25	< 1.0	13.8	33.3
	1	50	15.7	-	61.7
$Ce(AA)_3$	1	25	0	0	0
	1	50	0	< 1.0	29.4
$Ni(AA)_2$	1	25	3.7	-	22.5
	1	50	9.8	-	62.7
$Mn(AA)_3$	1	25	5.0	-	41.5
	1	50	23.6	38.8	> 99.0
SnOct	1	25	0	-	< 1.0
	1	50	< 1.0	5.7	13.8
$V(AA)_3$	1	25	0	-	< 1.0
	1	50	< 1.0	-	36.1
	2	25	0	-	2.5
	2	50	4.0	-	30.6
$VO(AA)_2$	1	25	0	-	< 1.0
	1	50	< 1.0	-	< 1.0
	2	25	0	-	16.7
	2	50	< 1.0	-	58.7
VONapthenate	1	25	0	-	< 1.0
	1	50	< 1.0	-	2.0
	2	25	0	-	< 1.0
	2	50	< 1.0	-	2.3
FeOct	1	25	35.7	-	77.3
	1	50	75.0	-	84.0
	2	25	51.3	-	83.3
	2	50	81.3	-	86.1
$In(AA)_4$	1	25	< 1.0	< 1.0	30.0
	1	50	-	36.1	44.8

TABLE I (Concluded)

Catalyst	Catalyst Level (wt. %)	Temperature (°C)	% Reaction		
			7 Days	14 Days	30 Days
V-neo-decanoate	2	25	< 1.0	-	8.9
	1	25	< 1.0	-	0
	1	25	< 1.0	-	5.3
Dibutyltin diacetate	1	25	0	-	< 1.0
	1	50	0	-	< 1.0
Tetra-n-butyltin	1	25	< 1.0	-	5.7
	1	50	10.5	-	20.3
Triphenyllead chloride	1	25	0	0	-
	1	50	0	t[c]/	-
Diphenyllead dichloride	1	25	0	0	-
	1	50	0	t	-
Tetraphenyllead	1	25	0	0	-
	1	50	0	t	-
Lead octoate	1	25	0	0	-
	1	50	0	t	-
Tetraphenylgermanium	1	25	0	0	-
	1	50	0	t	-
Cobaltocene	1	50	55.5/47.2[b]/	66.6/-	-

a/ Percent reaction is given as the average of the percent composition of the reactants within error limits.

b/ Deviation in stoichiometry noted; epoxide/acid.

c/ t = Trace.

The bulk of the other materials examined performed poorly as rate accelerators for the epoxide-carboxylic acid reaction. Elevated temperature is required to bring these reactions close to completion in 30 days. The ambient temperature runs had reacted only to the extent of 10 to 15% in 10 days. In general, the chelates (AA) are better catalysts than the salts for members of this group. There appears to be an induction period for some of these materials, especially chromium acetylacetonate. Mechanistically, this induction period may be the time required for the chelate to "open" and allow coordination of the reactants. Several of the materials falling into the "poor" category were reexamined with more attention being paid to examining the induction period. The results of the duplicate studies were in agreement with the previous results for the materials examined, i.e., they are poor catalysts, especially at ambient temperature. Doubling the amount of the materials used, e.g., manganese octoate, made no difference in the reaction rate at ambient and increased it only slightly at 50°C.

A series of vanadium and vanadyl (VO^{+2}) derivatives were also shown to be poor rate enhancers for the AGE-EHA reaction.

Stannous octoate is reported to be a good catalyst for the anhydride-epoxide copolymerization reaction at low and ambient temperatures. In the AGE-EHA system (as well as Telagen CT and ERLA-0510) it is a poor reaction promoter. Several other tin compounds were investigated to determine if this class of materials (nontransition) can be as effective in the carboxylic ester system as they are in the urethane. The results, once again have been disappointing. Those materials examined displayed poor rate enhancement properties.

To recapitulate, chromium salts were shown to be the best rate enhancers for the epoxide-acid reaction, with iron salts providing an intermediate category of catalysts worthy of continued evaluation. All other materials tested, including chelates and salts, are poor rate promoters at ambient temperature compared to the first two categories. As will be discussed later, these results were also verified in the binder studies. The chromium and iron salts were then subjected to more detailed kinetic analysis as described below.

D. Baseline Interactions in the Model Epoxide Acid Systems

The intent of the model systems studies was to provide a rapid and simplified means for screening catalysts in a relative sense insofar as they affect the rate and stoichiometry of the reaction. In other words, the desired result of these screening studies was to examine only the reaction of the cure functionalities and any alteration in reaction rate

10

and/or direction should be due to the catalysts and other known variables selected for evaluation. To determine those parameters within the model reaction system which have significant effects on the rate and direction of the main reaction, a single factorial experiment was designed to establish the existence of any parameter interplay. Model compounds of several different structures were employed: 2-ethyl hexanoic acid, octanoic acid (OA), allyl glycidyl ether (AGE) and epoxy butane (EB). The results of this study are shown in Table II. The responses used for the factorial experiments were percent reaction occurring in a 24-hr. period and the stoichiometric factor as defined in Footnote B, Table II. It was anticipated that only temperature and the presence of catalyst would affect the rate and direction of the reaction. Indeed, this was shown to be the case. Using the Yates method for analyzing the results of a factorial experiment (Ref. 2), the one most significant parameter (within the context of the matrix design used) for determining reaction rate is the presence or absence of catalysis. Temperature is the most important secondary parameter; however, compared to catalysis it is not statistically significant (once again, this conclusion is based on the statistical evaluation of the total matrix shown in Table II). When the experiment is reconsidered in light of the factors of major importance in the catalyzed system, examination of data in Table II shows that temperature is the most significant parameter. Acid structure appears to be affecting reaction rate also, though based on the data available this cannot be stated unequivocally. When octanoic acid is the substrate rather than 2-ethyl hexanoic acid, reaction goes approximately 20% faster at room temperature. At 50°C the rates follow the same trend but are too close in value to be used as the basis for any firm conclusion. Uncatalyzed, AGE-EHA react at 100°C; in 48 hr., 13.8% reaction has occurred with a stoichiometry of 1.

Reaction stoichiometry appears dependent on the type of acid used, the alpha-substituted EHA giving only one product while n-octanoic acid consistently gave a minor product amounting to nearly 3% of the product in some cases.

Since the relationship of acid and epoxide structures to reaction rate and direction is one of obvious importance, in both a mechanistic and a practical sense, further study was given to the rate and stoichiometric parameters in the solution reaction system. The results of the initial factorial experiment suggest that reaction stoichiometry is a function of acid type rather than a catalyst parameter at least in the chromium salt system). Table III and Figure 1 show the results of a series of experiments designed to change the reaction rate in the octanoic acid--AGE system, by either thermal or diffusional means. Only one side product was observed and its amount was always less than 2% of the total yield. These values are within the range of experimental error and no significance can be attributed to variations among them.

11

TABLE II

BASELINE INTERACTIONS FOR THE EPOXIDE-CARBOXYLIC ACID REACTION

Curing Agent Acid Structure

Temperature (°C)	Catalysis	Allyl Glycidyl Ether		Epoxy Butane	
		EHA	OA	EHA	OA
25	CrOct Present	AGE/EHA/RT/Cat % RXN a/ Stoich b/ 40.2 1	AGE/OA/RT/Cat 0.973 48.0 (0.027)	EB/EHA/RT/Cat 1 43.2	EB/OA/RT/Cat 0.975 50.4 (0.025)
	Absent	AGE/EHA/RT/No - 0	AGE/OA/RT/No - 0	EB/EHA/RT/No - 0	EB/OA/RT/No - 0
50	CrOct Present	AGE/EHA/50/Cat 1 95.9	AGE/OA/50/Cat 0.990 99.3 (0.010)	EB/EHA/50/Cat 1 97.2	EB/OA/50/Cat 0.984 98.5 (0.016)
	Absent	AGE/EHA/50/No - 0	AGE/OA/50/No - 0	EB/EHA/50/No - 0	EB/OA/50/No - 0

a/ Percent RXN in 24-hr. period as measured by the average consumption of starting material within experimental error limits.

b/ Stoichiometry is determined by the number of products noted in GC; product composition is determined relative to total area for products only. Hence, only one product would give a stoichiometric value of 1, a mixture of 98% major product, and 1.5 and 0.5% minor products, respectively, would be reported as an overall stoichiometry of 0.98 with the amounts of secondary products noted in parentheses, e.g., 0.980 (0.015, 0.005).

12

TABLE III

RATE-STOICHIOMETRY STUDY FOR OCTANOIC ACID AND AGE CATALYZED BY CrOct

Catalyst Level (wt. %)	Agitation[a]	Temperature (°C)	Time	Reaction (%)	Stoichiometry[b]
1	None	4	4 hr.	5.5	
	None		5 hr.	8.3	
	None		23 hr.	16.6	
	None		48 hr.	38.8	
	None		125 hr.	66.6	
	None		197 hr.	79.1	
	None		12 days	91.6	0.984 (0.016)
2	Shaker	25	5 hr.	40.3	
	Shaker		25 hr.	99+	
	Shaker		52 hr.	100	0.980 (0.020)
1	Shaker	25	4.5 hr.	19.4	
	Shaker		22.0 hr.	77.7	
			48.0 hr.	94.4	0.986 (0.014)

a/ In the standard experimental procedures the reaction systems are neither stirred nor agitated.

b/ With recorder sensitivity at maximum only one side product was noted; values noted in table were derived from data taken under normal operating conditions.
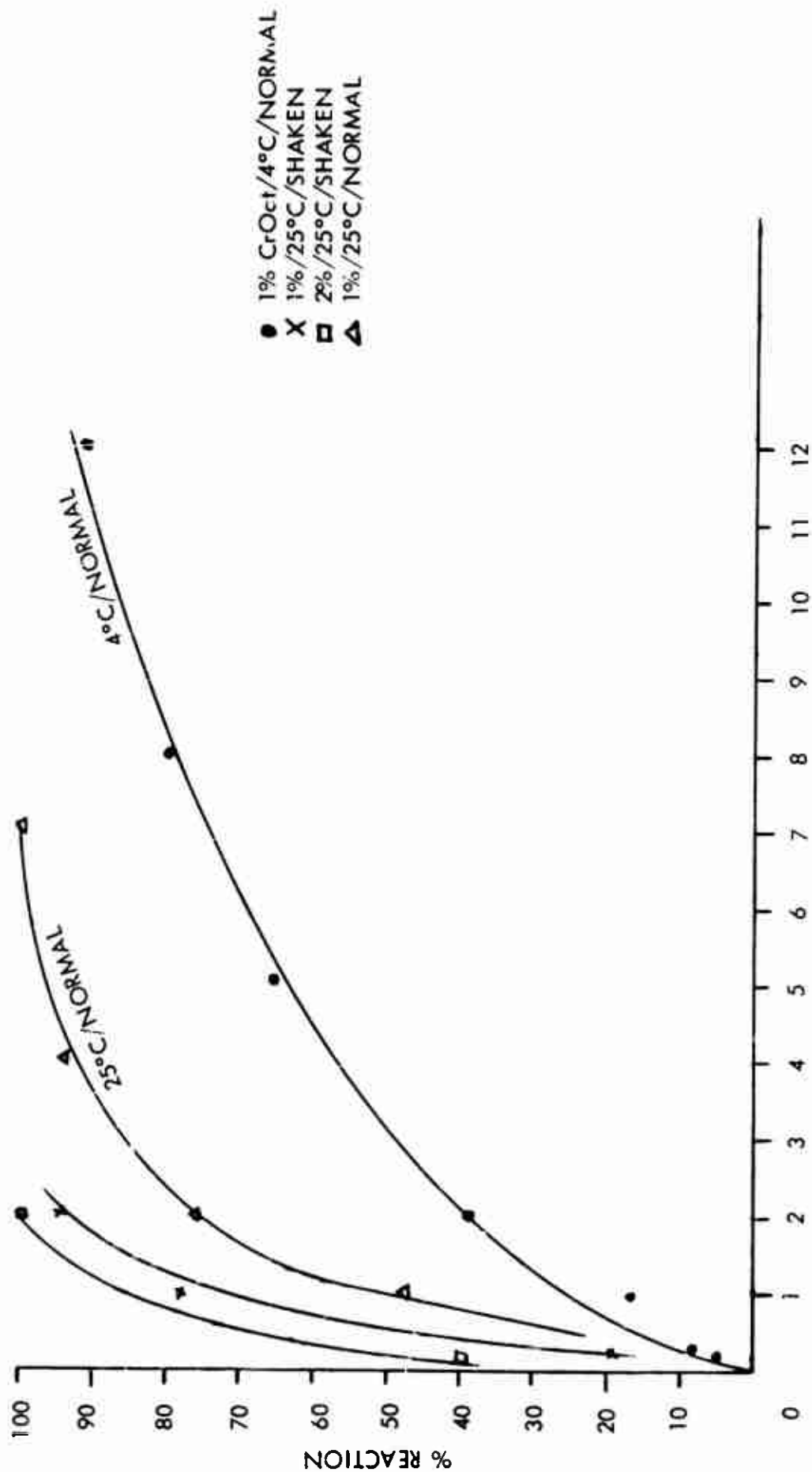
Figure 1 - Effect of Thermal and Agitation Conditions on the CrOct
Catalyzed Reaction of OA and AGE

14

The results of this experiment do indicate that product distribution under low temperature conditions is not a function of reaction rate.

The OA-AGE condensation reaction catalyzed by CrOct was then run under toluene reflux conditions, i.e., 110°C. In this situation only one side product was noted; however, it comprised 22% of the total yield. These results indicate that the reaction sequence leading to the forma'·n of the side product is a higher energy process than that leading to the main product.

Acid molecular weight may also be a key factor controlling both reaction rate and stoichiometry in solution. The smaller the acid, the greater would be its diffusional rate and hence reaction rate. In addition a smaller acid (than OA or EHA) would have a greater tendency to overcome steric hindrance at various reaction sites. Hence, for an acid of molecular weight lower than AGE (or OA), the rate of conversion should be faster and a greater number of products should form. This was found to be the case for propionic acid (PA) Table IV). Figure 2 shows a comparison of the reaction rate profiles for PA-AGE under various conditions and that for EHA-AGE. Under comparable conditions, the propionic system undergoes complete reaction significantly faster than the ethyl hexanoic mixture. Reaction stoichiometry is good with the major component forming 99% of the product. A widely varying number of side products is formed under the different conditions described with the greatest multiplicity being produced at elevated temperature (see Table IV). It should be noted that these products are present as trace quantities and their total in any given PA system was always less than 1%. This trend was also verified with valeric acid (C_5). In this case a total of two side products in less than 1% total quantity was noted.

Figure 3 is a schematic representation of the direction which can be taken by the catalyzed reaction of a monofunctional epoxide with monofunctional carboxylic acid. Compounds I and III are the expected major products of the reaction, that is, epoxides should be attacked at the least hindered carbon. Side products formed through attack on the other epoxide carbon are II and IV. Continued reaction of the hydroxyl group of the product ester with acid would lead to Compounds Ia, IIa, IIIa, and IVa. The results reported in Table II show that EHA gives only the major product while OA gives a mixture of products containing approximately 3% minor ingredient, which, for purposes of this discussion,will be assumed to be IV. The simplest explanation for this behavior is in terms of steric effects. EHA with its ethyl group adjacent to the reacting functionality will be directed toward the least crowded reaction path, i.e., the unsubstituted carbon of the epoxide. These steric effects may take on added importance since the reaction occurs through a catalytic intermediate. Octanoic acid does not possess this steric limitation and hence, a minor amount can "fit into" the reaction site around the substituted carbon of the epoxide.

15

TABLE IV

RATE DATA FOR PROPIONIC ACID - AGE
REACTION[a] CATALYZED BY CrOct

Catalyst Level (wt. %)	Temperature (°C)	Time (hr.)	Reaction (%)	Stoichiometry[b]
1	4	3.8	22.4	-
	4	22.5	36.7	-
	4	52.0	40.8	-
	4	144.0	75.5	0.99 + 2 minor
1	25	4.25	32.6	-
	25	28.0	88.7	0.99 + 3 minor
1	50	2.5	59.1	-
	50	5.5	86.7	-
	50	30.0	100.0	0.99 + 9 minor
2	25	4.5	54.0	-
	25	28.5	100.0	0.99 + 2 minor
2	50	2.5	91.8	-
	50	5.5	100.0	0.99 + 4 minor

a/   Reaction system consisted of equimolar amounts of acid and epoxide and
     an amount of toluene equal to the weight of both reactants.

b/   Reaction stoichiometry - only one side product is observed with recorder
     operating under normal conditions. At maximum sensitivity, a multiplic-
     ity of side products can be found; these, however, account for less
     than 1% of the total product.
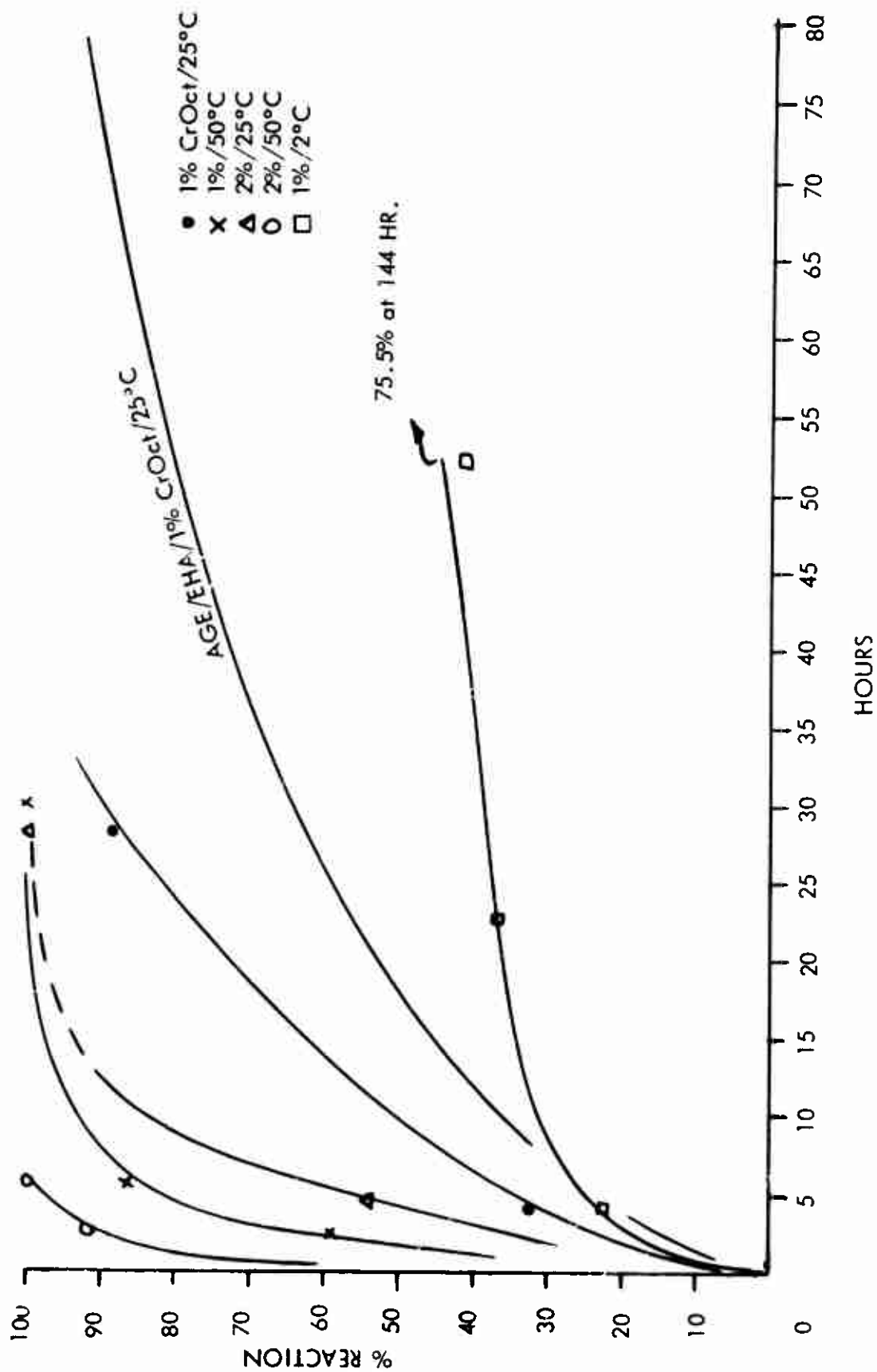
Figure 2 - Reaction Rate for Propionic Acid-AGE Reaction as a Function of Catalyst Quantity and Temperature

Figure 3 - Possible Reaction Paths in the Model Compound Studies

Should reaction continue through esterification of the product hydroxyl group, these steric factors would continue to govern product distribution. Ethyl hexanoic acid would be less inclined to react with its primary product because the hydroxyl group in question is in a secondary position along the carbon backbone, i.e., somewhat hindered. The primary, side chain hydroxyl group (as in II and IV) would seem to be a better target for continued reaction. Compound IV has not been observed; hence this continued reaction may not occur in the EHA system. For octanoic acid, both Ia and IIa are possible. Compound IIa may be sterically favored, but on a statistical basis more of Ia may form (since there is an abundance of I compared to II). The data reported in Table II show that only two products have thus far formed. The multiplicity of products formed when propionic acid or valeric acid is substituted for the C_8 acids used in the factorial study tends to support this mechanistic hypothesis. Both propionic and valeric acids are unhindered and smaller than either OA or EHA, and would be even less subject to steric control. Hence, a greater number of side products can result.

Homopolymerization of the epoxide is another factor which was evaluated to insure accurate interpretation of the results from the model systems studies. A series of potential catalysts (CrOct, CrOleate, Cr-neo-decanoate, MnOct, $Fe(AA)_3$, $Cr(AA)_3$, NiOct) were placed in the reaction system less acid, i.e., allyl glycidyl ether or epoxy butane in toluene, and subjected to 50°C. Compositions were monitored periodically by GC. No evidence was found for homopolymerization, i.e., no new products formed nor was there a decrease in the amount of epoxide content during a 14-day period. It was concluded that homopolymerization of the model epoxides in the presence of the catalysts does not occur under screening test conditions, i.e., 25° and 50°C in toluene solution.

Several conclusions about the nature and value of the solution condensation reaction can be made: (1) the reaction of AGE and EHA is stoichiometric and this system is suitable for the comparative screening of potential catalytic materials; (2) side reactions in the simplified model system are relatively unimportant; (3) there is a delicate balance among such parameters as acid molecular weight, carboxyl group environment, and product stoichiometry; and (4) the nature of the epoxide group, at least in the model system studies, appears to have little or no effect on the outcome of the reaction.

E. Summary of Catalyst Screening and Selection Studies

A large number of organometallic materials were screened in model system studies to assess their utility as potential cure catalysts for the carboxylic acid-epoxide binder. The materials fall into three categories with catalytic activity. Chromium salts (e.g., octoate, neodecanoate, oleate) were found to be excellent catalysts for converting carboxylic

19

acid and epoxide to ester. They gave complete stoichiometric reactions at room temperature in less than 7 days (in model systems). An intermediate group, composed of iron salts, gave approximately 70% reaction completion in 14 days at room temperature with 99% stoichiometry at this level of reaction. There is some question about the overall utility of the iron salts as cure catalysts because of the rate plateau observed and the deviation from stoichiometry observed during the later stages of reaction. All of the other materials evaluated as potential catalysts for the epoxide-carboxylic acid reaction were found to be poor rate accelerators at room temperature. In general, to reach 50% conversion a time period of 30 days at 50°C was required.

Hence, the chromium salts were selected for further development with CrOct as the major candidate. This material shows a good balance between solubility and chromium content, and it is commercially available at a reasonable cost. The chromium salts in general have thus far met the criteria for a cure catalyst in the epoxide-carboxylic acid binder system. They are catalytically active (once again especially CrOct) in low concentrations and give the desired reaction stoichiometry. As the result of this evaluation, CrOct was selected for evaluation in binder gumstocks and processing studies at ABL.

III.

CATALYST DESIGN AND REACTION MECHANISMS STUDIES

A. Objective

The objectives of these studies are to understand the factors controlling the behavior of the cure reaction (i.e., rate and direction) and the utilization of this information to optimize cure catalyst design. The mechanism and kinetics of the cure reaction is affected by such parameters as the nature and structure of the catalyst, the structures and steric environment of the reacting functionalities, temperature, contaminants, and type and level of solids loading.

B. Chromium Salts Studies

Based on the results of the screening studies, the chromium salts and soaps were selected for a more detailed evaluation of their chemistries as catalysts, their behavior in the presence of other propellant components and contaminants, and their behavior in binder and propellant systems. Of the commercially available chromium salts listed in Table V, chromium 2-ethyl hexanoate gave the greatest degree of rate enhancement. Examination of Table V gives an insight into the reasons for the differences in rates among the various chromium salts. It can be seen that the octoates as compared to the other commercially available chromium salts shown in Table V have higher percentages of chromium metal present per mole of material. Rate profiles for this and other chromium salts as functions of temperature and catalyst loading are shown in Figures 4, 5, and 6. The rate behaviors of the various chromium salts follow the same general pattern. As would be expected, the slowest segment of the reaction occurs during the last 10% conversion. The difficulty of this final conversion increases with decreasing amounts of catalyst. The reaction rate during the latter stages of the conversion is diffusion controlled. Hence, rates become increasingly slower as more of the reactants are consumed. Diffusion of curative and catalyst is an even more important rate parameter in the binder system than in the solution reaction. Continued reaction creates a solid matrix and the hindrance to reactant diffusion is drastically increased compared to the situation in the test solution. The catalysis of the final segment of the reaction should be enhanced by a catalyst of low molecular weight, which would be better able to diffuse throughout the matrix.

21

TABLE V

CHARACTERISTICS OF CHROMIUM SALTS

	Structure	Wt. % Cr[a]	Solubility[b] Characteristics
Oleate[c]	$C_8H_{17}CH=CH(CH_2)_7CO_2\ _3Cr$	5.7	Excellent
ne Decanoate[c]	$(CH_3(CH_2)_5C(CH_3)_2CO_2)_3Cr$	9.2	Excellent
Decanoate	$(CH_3(CH_2)_8CO_2)_3Cr$	9.2	Acceptable
Octanoate	$(CH_3(CH_2)_6CO_2)_3Cr$	10.7	Acceptable
2-Ethyl Hexanoate[c]	$(CH_3(CH_2)_3CHCO_2)_3Cr$ $\quad\quad\quad C_2H_5$	10.7	Good
Heptanoate	$(CH_3(CH_2)_5CO_2)_3Cr$	11.9	Good-Acceptable
Hexanoate	$(CH_3(CH_2)_4CO_2)_3Cr$	13.2	Poor
Acetate[c]	$(CH_3CO_2)_3Cr$	22.7	Insoluble
Formate[c]	$(HCO_2)_3Cr$	27.8	Insoluble

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a/ Stoichiometric amount; weight percent Cr in compound. Soaps are also
   available containing diluent or residual acid; in that case Cr con-
   tent is given as the percent of the total sample (including diluent).

b/ The evaluation of salt solubility is qualitative, based on ease of
   handling and solution of the catalyst in polymers as well as common
   solvents such as toluene, ethanol, acetone, methylene chloride, and
   tetrahydrofuran.

c/ Commercially available.
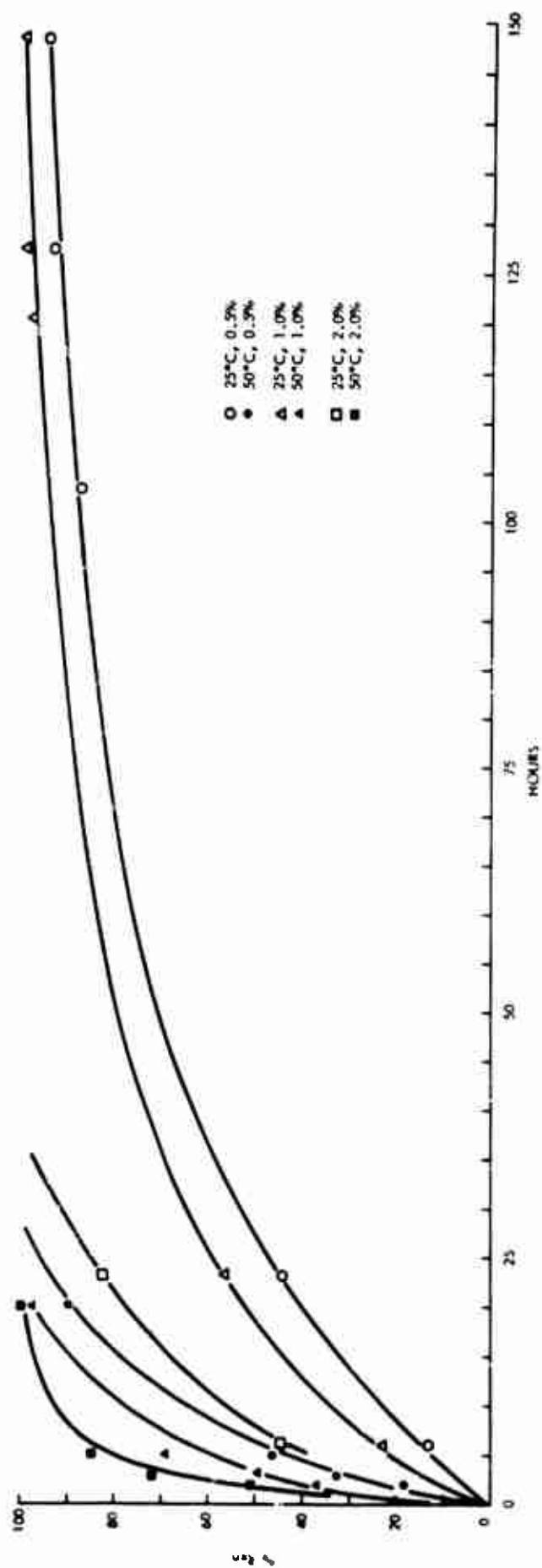
Figure 4 - Rate of EHA-AGE Reaction as a Function of CrOct Catalyst Quantity and Temperature

23
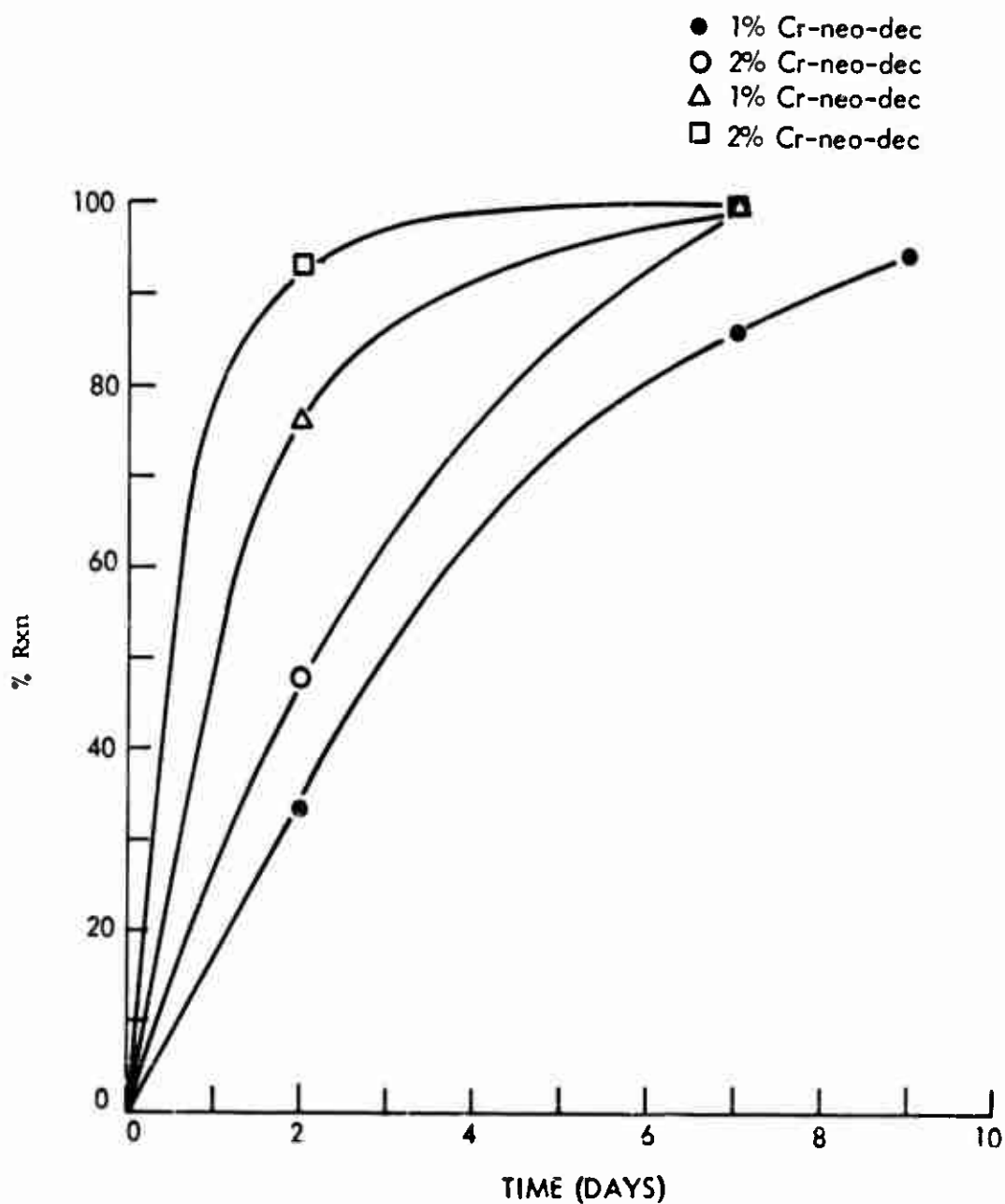
Figure 5 - The Effect of Temperature and Catalyst Quantity on the
Cr-neo-decanoate Catalyzed Reaction of AGE and EHA
(catalyst is 5.0% Cr-neo-decanoate, that is, less
than stoichiometric; see Table V)
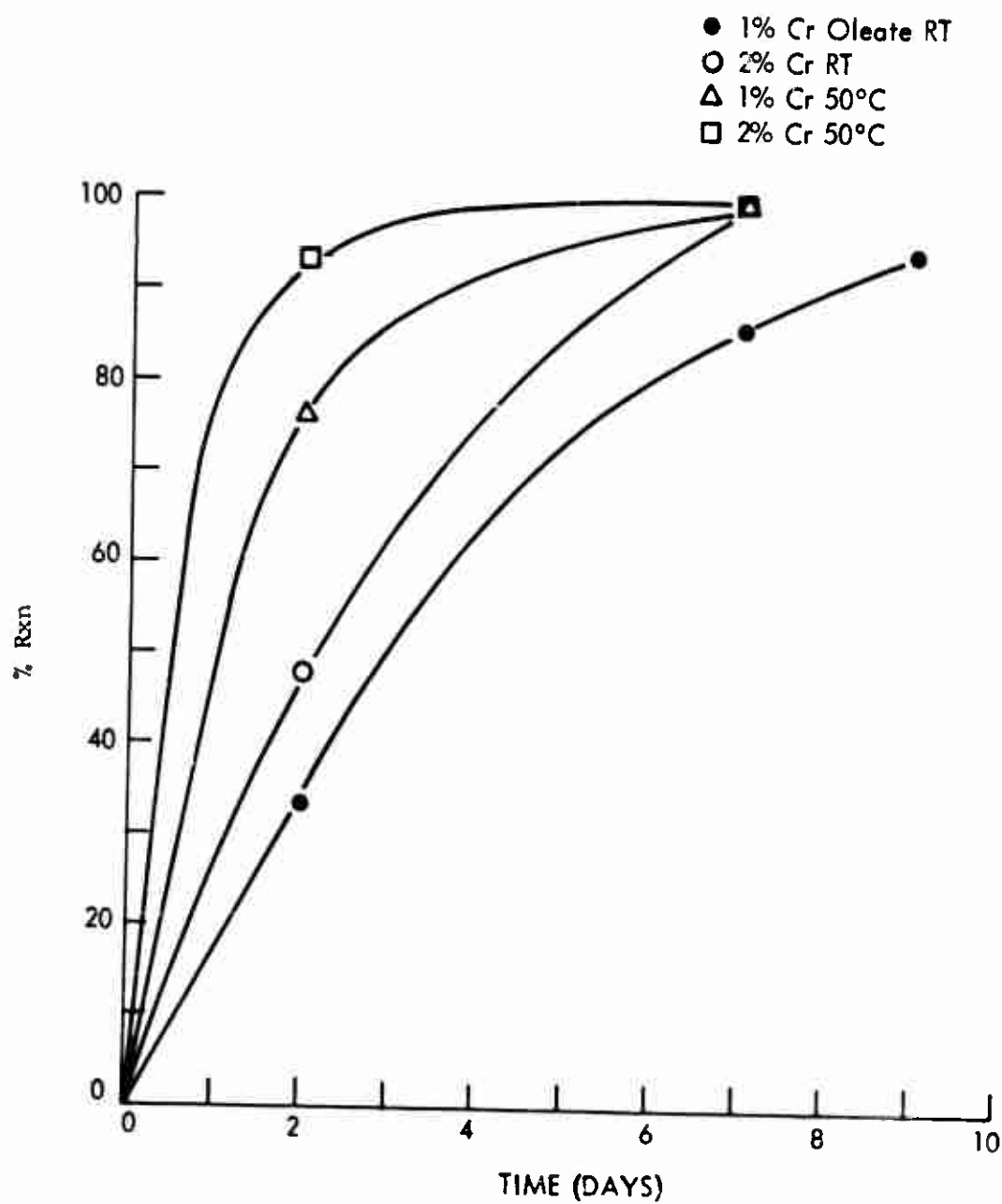
Figure 6 - The Effect of Temperature and Catalyst Quantity on Cr Oleate Catalyzed Reaction of AGE and EHA

These results suggest at least three key rate determining parameters for the chromium soap catalysts: (1) chromium content of a given compound (the higher the metal content the faster the conversion, e.g., CrOct vs. CrOleate); (2) solubility of the Cr material in the reaction medium (binder mix or solution); and (3) as will be discussed below, steric environment around the carboxyl group of the organic portion of the metal salt. Table V shows some of the structural characteristics of a number of Cr salts.

Theory would suggest that the steric environment within the catalyst itself may have an effect on the conversion rate of the acid-epoxide reaction. Table VI lists rate data for the reaction of AGE and EHA catalyzed by chromium heptanoate and hexanoate. The chromium heptanoate analyzed at 8.45% chromium (11.80% is theoretical), indicating the sample to contain 28.3% free heptanoic acid.

TABLE VI

CATALYSIS BY Cr HEPTANOATE AND HEXANOATE

Catalyst	Catalyst Level (wt. %)	Temp. (°C)	Time (hr.)	% Rxn
Cr Heptanoate[a]/	1	25	19	42.6
			22	50.0
			43	83.8
			48	97.1
	1	50	1	13.2
			3.8	70.5
			5.8	82.4
			23	99.0+
Cr Hexanoate[b]/	1	25	21	13.2
			45	27.9
			69	45.5
			30 days	100.0
	1	50	3	33.8
			4	38.2
			6	47.1
			23	99.0+

a/ Sample contained 71.7% salt and 28.3% free acid; hence, catalyst sample contained 8.46% Cr.

b/ Sample contained 43% titratable acid; hence, Cr content is 5.67%.

26

Table VII shows a comparison of rate data for identical AGE/EHA reaction systems catalyzed by chromium octoate and chromium heptanoate. Consider the following relationships:

$$\text{Catalyst ratio:} \quad \frac{\text{CrHep}}{\text{CrOct}} = \frac{7.1}{9.2} = 0.771$$

$$\text{Time to 50\% conversion:} \quad \frac{\text{CrHep}}{\text{CrOct}} = \frac{22}{20} = 1.1; \text{ inverse } 0.91$$

Comparing the ratios for a situation of equal 50% conversion times, 0.845 mole of chromium heptanoate would equal 1 mole of chromium octoate in catalyzing ability. This exercise may oversimplify the kinetic situation; however, suffice it to say that chromium heptanoate gives better rate acceleration than chromium octoate on a mole-for-mole basis in a completely miscible system.

TABLE VII

RELATIONSHIP OF CATALYST QUANTITY AND RATE
FOR Cr OCTOATE AND HEPTANOATE

Catalyst	Time to 50% Conversion (hr.)	Amount of Catalyst Present (moles)	Grams Cr Present
CrOct	20	9.2×10^{-5}	0.0047
Cr Heptanoate	22	7.1×10^{-5}	0.0037

The difference in activity displayed by the two catalysts may be due to the presence of the ethyl group at the two-position in the CrOct organic ligand which would hinder (relative to the unsubstituted situation) the approach of the reactant carboxylic acid group to the chromium nucleus for activation purposes. Hence, a given acid can reach the chromium easier in chromium heptanoate than it can in chromium octoate (the octoate group being 2-ethyl hexanoate).

The low purity of the hexanoate sample precluded a similar comparison to other chromium catalysts.

C. Substrate Steric Parameters

Early work on this program suggested that reaction rate and direction were functions of acid type rather than of catalyst parameters.* Further studies have supported the acid structure rate contention; however, the nature of the organic group in the metal catalyst has also been shown to alter conversion rate.

Concerning acid steric control, two mixed-acid systems catalyzed by a 1% loading of CrOct were examined: (1) equimolar amounts of octanoic acid and 2-ethyl hexanoic acid were reacted with an equivalent amount of allyl glycidyl ether (equivalent amounts of total acid and epoxide); (2) equimolar amounts of 2-ethyl hexanoic and propionic acids with an equivalent amount of allyl glycidyl ether. The rate data for these reactions are given in Table VIII, and Figures 7 and 8 show rate profile plots for these results.

The least sterically hindered acids (OA, PA) and the lower molecular weight acid (PA) always reacted faster than the α-substituted EHA. The most revealing comparisons result from an examination of the conversion data for the OA and EHA experiment where molecular weight is not a competitive parameter. Table IX shows the data for time to 50% conversion of the two acids with AGE in the presence of CrOct.

Analysis of these data shows correlation of reaction rate with steric effects. In the mixed acid system OA reaches the 50% consumption point in 5 hr. When OA is the only acid, 2% catalyst loading is required for the same equivalence level (CO_2H/epoxide) to give 50% conversion of OA in the same time period. Hence, the steric factors are compelling enough to virtually exclude EHA from activation by the catalyst until OA is consumed (hence, OA "sees" the catalyst level as 2% instead of 1).

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* α-Substituted acids give slower reaction rates than unsubstituted ones but give only one product while the unsubstituted acid gives a side product amounting to 2-5% depending on conditions.

TABLE VIII

REACTION OF AGE WITH MIXED ACID[a] CATALYZED BY CrOct

Temperature (°C)	Catalyst Level (wt. %)	Time (hr.)	% Reaction[b]		
PA/EHA Series			AGE	PA	EHA
25	1	5	36.5	50.0	30.9
		24	85.4	95.2	76.7
		31	86.6	97.6	76.2
		49	95.1	100	90.5
50	1	1.5	46.3	62.0	35.7
		3	76.8	90.5	64.3
		6	87.8	95.2	80.9
		24	99+	100	99+
25	0.4	4.5	9.8	28.5	0
		26.5	45.1	61.9	35.7
		50.0	69.5	80.9	61.9
		76.0	81.7	100	69.0
		9 days	99+	100	99+
50	0.4	1	10.9	23.8	0
		2.5	14.9	28.5	0
		29	95.1	100	90.5
		53	98.7	100	97.6
		72	99+	100	99+
			AGE	OA	EHA
OA/EHA Series					
25	1	5	30.5	44.4	11.1
		25	73.6	91.6	55.5
		31	80.5	94.4	66.6
		52	92.7	100	85.5
		74	97.2	100	94.4
50	1	2	47.2	66.0	22.2
		4	70.8	91.5	50.0
		25	99+	100	99+
25	0.4	26	41.6	55.5	16.6
		48	59.7	77.7	44.4
		51	62.5	83.3	50.0
		76	75.0	91.0	63.5
		9 days	94.4	100	88.8
50	0.4	2	22.2	27.7	16.6
		4	41.6	72.2	16.6
		24	91.6	100	83.3
		29	93.0	100	86.1
		30	94.4	100	88.8
		48	97.2	100	94.4
		73	100	100	100

a/ Reaction mixtures consisted of equivalent amounts of epoxide and acid functionalities in the following molar ratios:
1 AGE/0.5PA/0.5EHA and 1 AGE/0.5OA/0.5EHA

b/ Percent reaction is given as the percent conversion of the given reactant; % AGE = % total conversion

$$\% \text{ AGE} = \frac{\% \text{ Acid}_A}{2} + \frac{\% \text{ Acid}_B}{2}$$

29
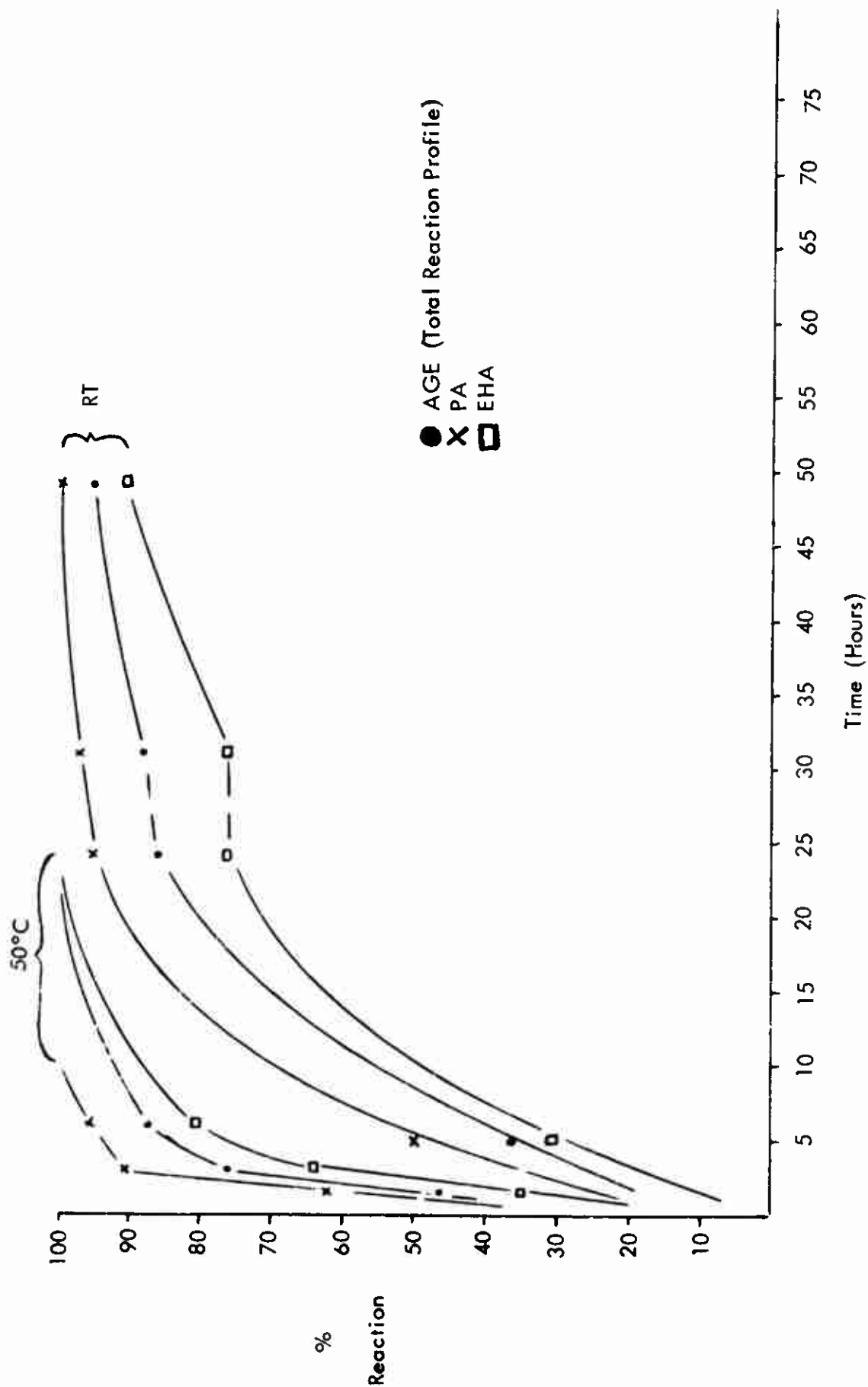
Figure 7 - Reaction Analysis - Mixed Acid System with AGE Catalyzed by 1% CrOct. Equivalent ratio: (1 AGE/0.5EHA/0.5PA)
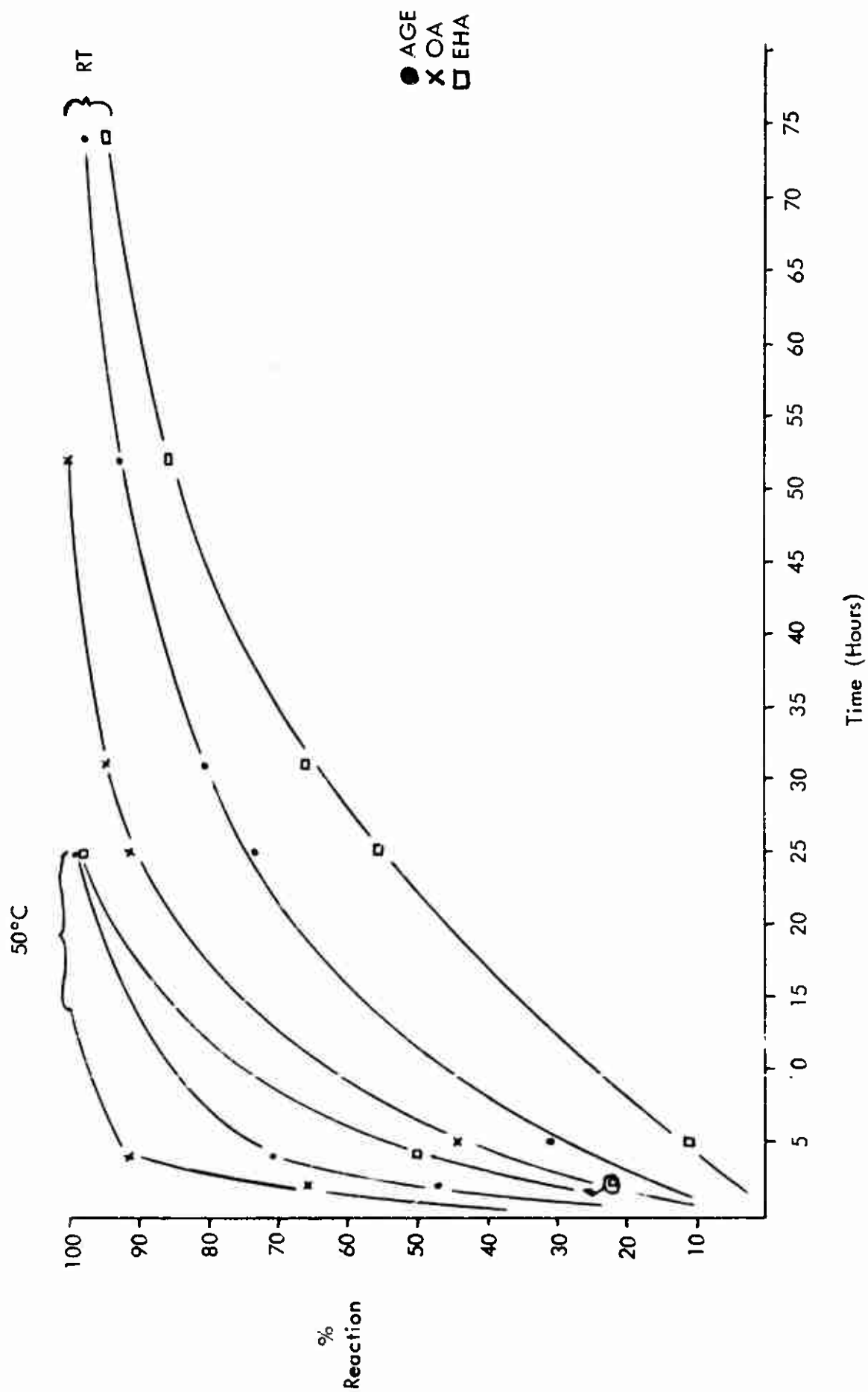
Figure 8 - Reaction Analysis - Mixed Acid System with AGE and 1% GrOct. Equivalent ratio: (1 AGE/0.50A/0.5EHA)

TABLE IX

RATE DATA FOR CONVERSION OF VARIOUS ACIDS WITH CrOct

Reaction System[a]	Temp. (°C)	Catalyst Level[b] Wt. %		Time to 50% Conversion (hr.)
AGE + OA	25	1		11.0
	25	2		5.5
AGE + EHA	25	1	OA	20.0
AGE + EHA/OA[c]	25	1	EHA	22.5

a/ Equivalent amounts of acid and epoxide in toluene solution.

b/ Catalyst level in wt. % of catalyst based on total reaction solution (including toluene).

c/ Reaction mixture consisted of equivalent amounts of epoxide and acid functionalities in the following molar ratios: 1 AGE/0.5 EHA/0.5 OA.

The following conclusions may be drawn concerning substrate acid structure rate effects: (1) where acid molecular weight is not a competitive parameter, as in the OA-EHA situation, steric crowding about the carboxylic acid group is a rate as well as stoichiometry controlling factor; (2) this conclusion can be extrapolated to the polymer situation, that is, where different types of acid groups are present in the prepolymer these will be consumed at different rates, and since binder reactions do not go to completion, the identity of the unreacted group can be predicted; (3) the nature of the catalytic intermediate (in at least the Cr system) is such that α-carbon substituents in the reactant acid are in proximity to the activation site (further supporting the contention that it is the acid which is activated during the catalysis step); (4) in terms of catalyst design, less bulky substituents in the organic portion of the catalyst may facilitate the reaction rate (a point discussed below); and (5) metal catalysis does not level the reaction rates of different carboxylic acid groups. Hence, in addition to acting as a carrier for the metal, the ligand plays a role in controlling reaction rate.

D. Variable Substrate Concentration Studies

To gain further insight into the mechanism of the catalyzed conversion and to determine the nature of those reactions which may be important in a post-cure sense, studies were undertaken in which the initial amounts of reactants were varied.

32

1.   Excess epoxide: Three separate systems were examined: (1) EHA
and twice the number of equivalents of AGE, (2) OA and twice the equiva-
lents of AGE, (3) separately prepared ester from AGE-EHA with an equiva-
lent amount of AGE. The results of the reactions are shown in Table X.
In the presence of CrOct, the carboxylic acid-epoxide addition reaction
is exclusive at 25, 50 and most probably 100°C. This can be seen from
the GC analysis in which acid and epoxide are consumed at equivalent
rates until all acid is consumed and no additional products are noted up
to this point relative to behavior of these two materials in the standard
reaction system (equivalent initial amounts of reactants). The rates of
reaction are those expected for the catalyst/reactant (acid) molar ratio
used. These results tend to support the notion that the key catalytic
interaction involves the carboxylic acid and the chromium salt.

Beyond the total acid consumption point, postesterification epoxide
consumption (with catalyst present) is very temperature dependent. Epoxide
loss does occur to a limited extent at 50°C ($\sim$ 15-20%) in 40 days. The
fact that only trace products were noted in the GC is most likely due
to the fact that they are of high molecular weight and not sensitive to
the method of analysis used. At 100°C nearly complete epoxide loss is
noted, accompanied by polymerization of the reaction system. Postesteri-
fication reaction at 25°C (in presence of Cr) is minor ($\sim$ 13% in 40 days).
The control experiment (ester/AGE/no catalyst/100°C) showed only minor
epoxide consumption (11% in 35 days) while similar reactions with Cr
catalyst present resulted in polymerization and high (85%) epoxide loss
in the same time interval.

Several conclusions may be drawn: (1) in the presence of diffusible
(excess or residual) epoxide, further reaction between epoxide and ester
product will occur (unreacted epoxide will be present in a propellant
matrix, however, it will be attached to a polyfunctional curative incor-
porated into the binder network and will be nondiffusable or only slightly
so in a reactivity sense); (2) the results (exclusive acid-epoxide reac-
tion until total consumption of acid) support the suggestion that the key
catalytic interaction involves carboxylic acid and the chromium species;
(4) chromium catalyst promotes the postesterification reaction of epoxide
and hydroxyl group of the product, and (5) this postesterification reaction
is important only at elevated temperatures (100°C) and does not appear
significant under ambient conditions.

2.   Excess acid studies: The effect of excess acid on the rate and di-
rection of the CrOct catalyzed cure reaction was examined in model systems
employing EHA-ACE mixtures 1.5:1 and 1.2:1 equivalent proportions at 25° and
50°C. As in the excess epoxide case, reaction is stoichiometric, i.e., acid
and epoxide disappear at equal rates. Unlike the excess epoxide situation,
however, no post-esterification reaction occurs in 35 days after completion
of the main reaction at either 25° or 50°C. Rate patterns (see Figure 9) are
within experimental error of the equivalent acid-epoxide reaction.

33

TABLE X

DATA SUMMARY

Excess Epoxide Experiment

System[a]	Catalyst	Time	Temperature (°C)	Observation	
				Product Formation (%)	Epoxide Consumption Beyond Complete Esterification

A. **Early Reaction Data**

System[a]	Catalyst	Time	Temperature (°C)	Product Formation (%)	Epoxide Consumption Beyond Complete Esterification
EHA(1)/ACE(2)	1% CrOct	6.8 hr.	25	32	-
		25.5 hr.	25	100	0
		7.0 days	25	100	13.0
		2.5 hr.	50	100	-
		24.5 hr.	50	100	0
		7.0 days	50	100	8.6
		1.0 hr.	100	100	8.6
		2.0 hr.	100	100	8.6
		3.0 hr.	100	100	8.6
		7.0 days	100	100	21.7
		13.0 days	100	100	43.4
OA(1)/ACE(1)	1% CrOct	6.5 hr.	25	58	-
		26.0 hr.	25	100	6.7
		9.0 days	25	100	8.5
		2.8 hr.	50	100	1.3
		25.0 hr.	50	100	6.2
		7.0 days	50	100	13.0
		1.0 hr.	100	100	2.2
		2.0 hr.	100	100	6.7
		3.0 hr.	100	100	11.6
		20.0 hr.	100	100	13.0
		6.0 days	100	100	24.6
		13.0 days	100	100	29.6
EHA Prod/ACE	1% CrOct	3.0 hr.	100	-	5.8
		20.0 hr.	100	-	44.7
		6.0 days	100	-	11.7
		13.0 days	100	-	14.7
		4.5 hr.	50	-	0
		25.4 hr.	50	-	0.8
		7.0 days	50	-	2.0
		6.0 hr.	25	-	0
		27.0 hr.	25	-	0
		9.0 days	25	-	0

a/ Numbers in parentheses refer to relative molar ratio of the two components.

TABLE X (Concluded)

B. Surveillance of Above Experiments

System	Catalyst (Wt. %)	Temperature (°C)	Time Days	Epoxide Consumption Beyond Ester Formation		
				G.C.	Titration	Comment
EHA(1)/	1% CrOct	25	7	13.0	-	
ACE(2)		25	22	14.0	-	No side prod.
		25	41	14.0	13.8	No side prod.
		50	7	8.6	-	
		50	22	15.3	-	
		50	40	20.5	22.3	Trace side prod.
		100	13	43.4	-	
		100	16	56.5	-	
		100	40	-	90.0	Polymerized
OA(1)/	1% CrOct	25	9	8.5		
ACE(2)		25	22	13.0	-	
		25	41	18.5	13.0	No side prod.
		50	7	13.0	-	
		50	22	15.0	-	
		50	40	-	17.7	
		100	13	29.0	-	
		100	16	80.0	-	2 major side prod.
		100	20	85.0	-	Polymerized
		100	40	-	92.6	Polymer
EHA Prod/	1% CrOct	28	9.0	0	-	
ACE		25	20.0	2.0	-	
		25	41.0	4.8	6.4	
		50	7.0	2.0	-	
		50	22.0	2.8	-	
		50	40.0	13.0	14.7	
		100	13.0	14.7	-	
		100	16.0	27.7	-	
		100	20.0	35.0	-	Side prod., brown, viscous
		100	40.0	-	100.0	Polymerized
Control:	No	100	1.0	0	-	
EHA Prod/	catalyst	100	5.0	0	-	
ACE		100	8.0	2.8	-	
		100	9.0	3.5	-	
		100	30.0	-	11.1	Slight yellowing, no polymerization
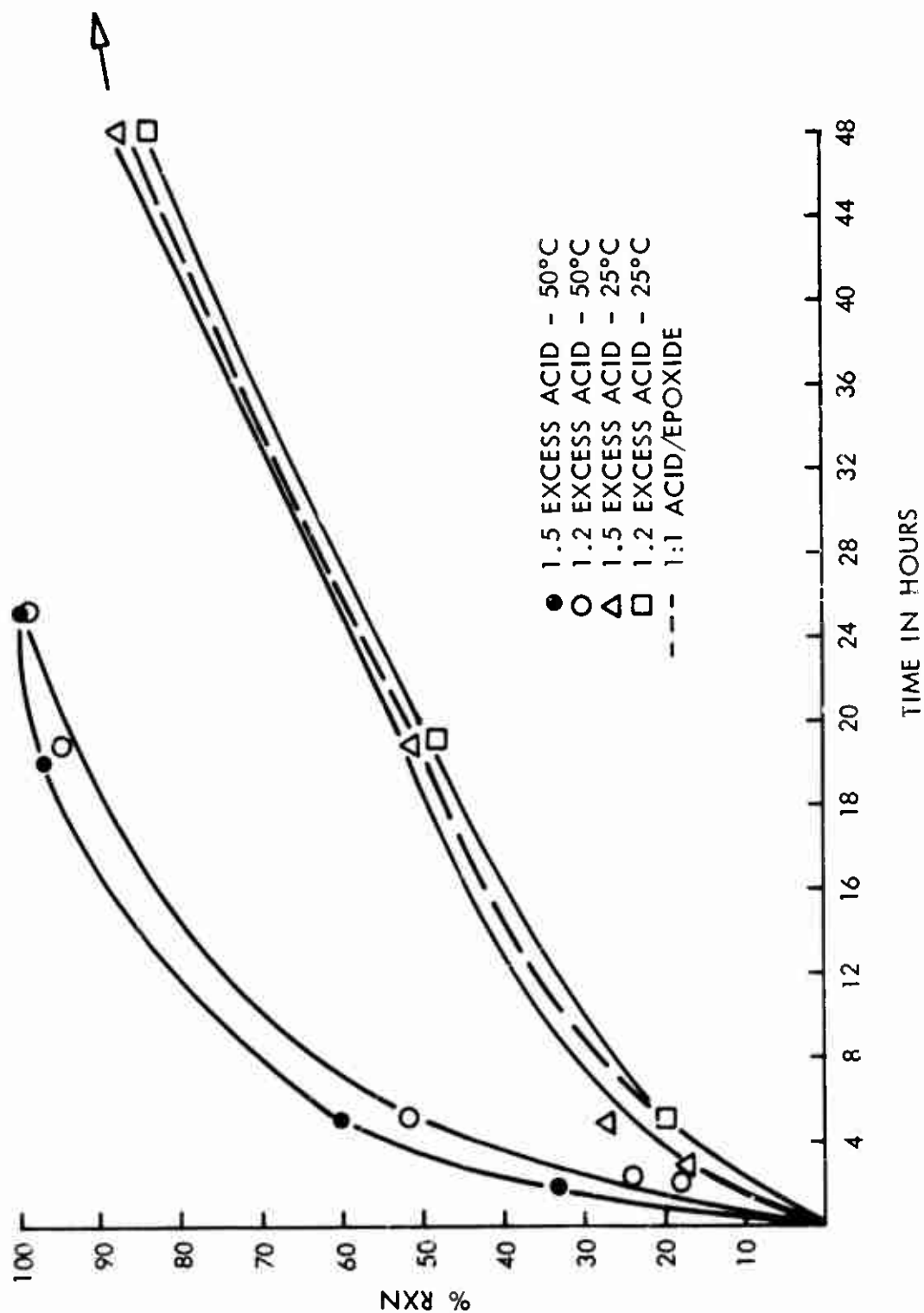
Figure 9 - Rate Patterns for Excess Acid Reactions; 1.5 Equivalents of EHA:1 Equivalent of AGE, and 1.2 EHA:1 AGE; 1% CrOct Catalyst Level

3. <u>Rate dependence on catalyst concentration</u>: The dependence of reaction rate on catalyst quantity is shown in Figure 10. The data from an experimental series in which catalyst concentration was the only reaction variable are shown in Table XI. Initial concentrations of reactants (epoxide and acid) are the same; the reaction is stoichiometric, i.e., $-d[CO_2H]/dt = -d[epoxide]/dt = +d[product]/dt$. The rate is expressed as the number of moles of product formed per hour at 50% conversion. Figure 3 is a log-log plot* of the reaction rate versus the ratio of molar concentrations of catalyst to reactant at fixed initial reactant concentrations. The plot is linear with a slope of one indicating first order dependence of reaction rate on catalyst concentration. Mechanistically, these results suggest the existence of a reactant-organometallic intermediate in the rate-controlling step for the conversion and are in agreement with the spectroscopic evidence indicating coordination of the chromium salt with carboxylic acid.

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* The log-log plot is based on the following derivation:

$$A + B + Cat \longrightarrow Products$$
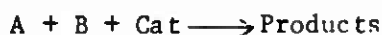
$$\frac{d[c]}{dt} = k\,[acid]\,[epoxide]\,[cat]$$

k, $[acid]$ and $[epoxide]$ are constant

$$\therefore k\,[acid]\,[epoxide] = K$$

$$\frac{d[c]}{dt} = K\,[cat]$$

$$let \quad \frac{d[c]}{dt} = R$$

$$R = K\,[cat]^{\,x}$$

$$\log R = x\,\log[cat] + \log K$$

The relationship is now expressed in straight line form, and x is the slope.
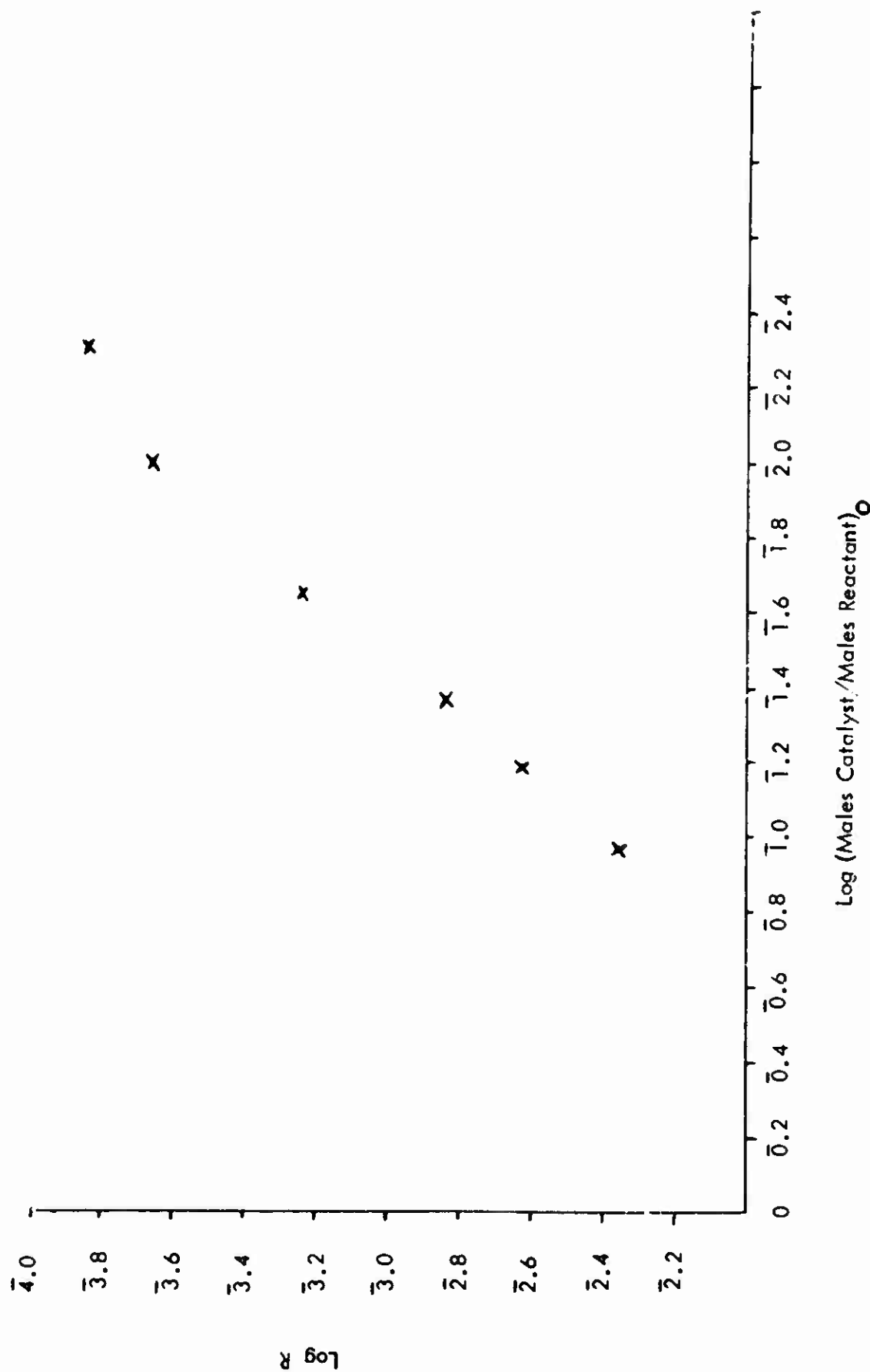
Figure 10 - Rate Dependence of Acid-Epoxide Reaction
on Catalyst Concentration

TABLE XI

KINETIC ANALYSIS RATE DEPENDENCE
ON CATALYST CONCENTRATION

EHA	Moles of Components AGE	CrOct	Molar Ratio Catalyst Reactant	Log Molar Ratio	Rate[a]/ d[c]/dt Moles/hr x 10^4	Log Rate
0.0086	0.0086	4.60×10^{-5} (0.5)[b]/	0.0053	$\bar{2}.2758$	1.43	$\bar{3}.38448$
0.0086	0.0086	9.24×10^{-5} (1)	0.0107	$\bar{1}.9706$	2.15	$\bar{3}.6676$
0.0086	0.0086	1.85×10^{-4} (2)	0.0215	$\bar{1}.6676$	5.73	$\bar{3}.2419$
0.0086	0.0086	3.69×10^{-4} (4)	0.0429	$\bar{1}.3675$	15.10	$\bar{2}.8211$
0.0086	0.0086	5.54×10^{-4} (6)	0.0644	$\bar{1}.1911$	24.00	$\bar{2}.6198$
0.0086	0.0086	9.24×10^{-4} (10)	0.1074	0.9690	43.00	$\bar{2}.3666$

a/ Rate = moles of product formed per hour in 0-50% reaction range.
b/ Number in parentheses refers to catalyst levels in reaction system expressed as weight percent.

39

E. Ferric Octoate Studies

From the results of the screening studies, ferric octoate appeared to be a good rate accelerator for the AGE-EHA reaction. However, a more detailed examination of its rate acceleration behavior shows that after approximately 60 to 70% conversion, a rate plateau is reached. This effect is noticeable at both 1 and 2% by weight catalyst levels, and elevated as well as ambient temperature. This thermal effect is strongly suggestive of a loss of catalytic activity by the iron compound. Indeed, examination of the sample vials shows a gelatinous precipitate present in the 2% sample and a color change in the 50°C runs. Of the material in solution, six minor products (each in trace quantities) amounting to approximately 2% of the total product were noted. The rate data for FeOct as a catalyst are shown in Figure 11; Table XII displays the results of the various reaction series run to examine the FeOct rate phenomena and to check its reproducibility. Analysis of the initial series after 60 and 88 days shows nearly total consumption of the epoxide while 20 to 30% of the acid remains unreacted. The side product formed by the extra consumption of epoxide is the precipitate observed previously, since GC analysis of the dissolved material shows no extraordinary deviations in reaction direction.

The side reaction behavior was noted also in solutions contaminated with water. Again, epoxide was consumed faster than acid and the threshold for this deviation in stoichiometry appears at 60 to 65% conversion.

There are at least two possibilities which would explain the side reaction: (1) an epoxide homopolymerization reaction which becomes important during the later stages of cure where the rate of ester formation slows down due to the decrease in reactant concentration and ensuing importance of diffusion; (2) reaction of epoxide with the catalyst itself due to the decrease in the amount of activated reactant acid.

An exploratory study was made using a mixed FeOct/CrOct catalyst (0.5/ 0.5% weight). The reaction behavior (that is, rate and stoichiometry) observed was that expected of the CrOct catalyst at the 0.5% level with a slight acceleratory assist from the FeOct (see Table XIII), thereby confirming the dominance of the catalytic effect of Cr even in the presence of potential reaction-promotion competitors.
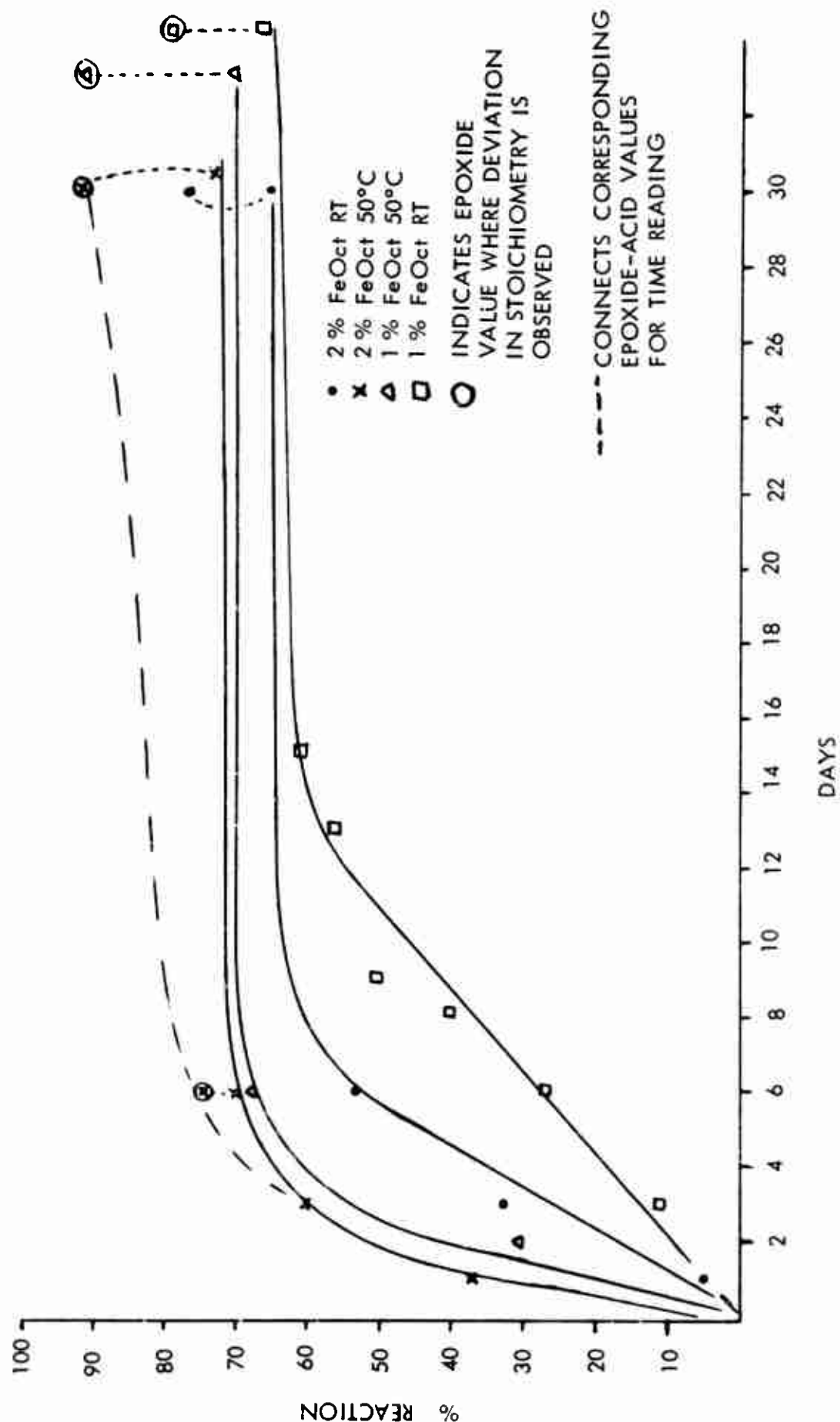
Figure 1i - The Effect of FeOct on the Rate and Stoichiometry of the AGE-EHA Reaction at Different Temperatures and Catalyst Levels

41

TABLE XII

FeOct STUDIES

		Level	Temperature	Time	Percent Reaction
A.	Rerun Series	2%	RT	2 hr.	> 1
				26 hr.	4.8
				3 days	32.9
				6 days	52.9
				30 days	{ Acid 65.2 / Epoxide 77.7
		2%	50°C	2.5 hr.	> 1
				1 day	37.1
				3 days	60.0
				6 days	70.0 (epoxide 74.2)
				30 days	{ Acid 72.2 / Epoxide 91.6
B.	Initial Series	2%	50°C	60 days	Acid 69.4 / Epoxide 97.2
		2%	RT	88 days	Acid 75.0 / Epoxide 97.2
		1%	50°C	60 days	Acid 69.4 / Epoxide 91.6
		1%	RT	88 days	Acid 66.6 / Epoxide 79.1

C. H_2O Effect Studies
   Catalyst Level

Level		Temperature	Time	Percent Reaction
2%	18 µl.	50°C	2.5 hr.	> 1
			24 hr.	28.5
			3 days	55.5
			6 days	61.1
			33 days	{ Acid 63.8 / Epoxide 95.8
2%	18 µl.	RT	2 hr.	> 1
			26 hr.	19.4
			3 days	34.7
			6 days	44.4
			33 days	{ Acid 72.2 / Epoxide 77.7

42

TABLE XIII

MIXED METAL OCTOATE CATALYST STUDIES[a]

Temperature	Time	Reaction (%)	Analogous 0.5% CrOct Reaction
RT	1 hr.	t	
	1 day	47.2	(43.9)
	3 days	86.1	(80.2)
	6 days	91.6	(94.3)
50°C	25 hr.	30.6	
	1 day	77.7	
	3 days	99+	
	6 days	100	

a/ Catalyst in this case was an equal weight mixture of CrOct and FeOct, that is, 0.5% CrOct and 0.5% FeOct by weight of the total reaction solution.

IV.

EXTRA INGREDIENT EFFECTS ON THE CHROMIUM SALT SYSTEMS

A. Propellant Components

The chromium salts are excellent catalysts for the carboxylic acid-epoxide reaction. To be successful as cure catalysts, they must demonstrate the same type of catalytic behavior in the propellant environment; i.e., they must promote the esterification reaction in the presence of other potentially reactive ingredients. CrOct, CrOleate, and Cr-neo-decanoate were selected for this evaluation, the octoate being the prime candidate while the other two are representative of the other types of chromium salts available.

1. Ammonium perchlorate: The introduction of 5% by weight of ammonium perchlorate into the standard test system (ACE-EHA-toluene-CrOct) does not alter the rate or stoichiometric outcome of the condensation reaction at either ambient temperature or 50°C. These data are presented in Table XIIIa and plotted relative to the behavior of the reaction system without AP in Figure 12. All points fall on their respective temperature plots. It is concluded that AP, in this weight percent range at least, does not alter the outcome of the solution reaction. The completed reactions containing ammonium perchlorate, catalyst, and product ester were set aside and monitored throughout the course of the program to determine the long-range effects of AP in the presence of CrOct on the stability of the ester linkage.

2. Additional propellant solids: Table XIV lists several other propellant ingredients whose effect on the catalyzed AGE-EHA reaction was examined. One surfactant and two antioxidants were included: Roccal (a quaternary ammonium salt), AO-2246, and phenyl-β-naphthylamine, respectively. The results of these experiments are displayed in Figures 13 and 14. No alteration in reaction direction was noted for the reactions catalyzed by CrOct and Cr-neo-decanoate. Considering the CrOct case first, the rate of ester formation was only slightly accelerated by the presence of the extra ingredient, and in many cases, it is doubtful whether the differences relative to the baseline cure (CrOct alone) are real. Only phenyl-β-naphthylamine appears to give a definite reaction rate increase (12% more conversion after 24 hr.).

An acceleratory effect by the antioxidants would not be surprising, especially at the concentration levels being used (0.5% by weight, or half as much by weight as the cure catalyst). The antioxidants are amines, and hence have catalytic properties toward the acid-epoxide reaction.

44

TABLE XIIIa

THE EFFECT OF AMMONIUM PERCHLORATE ON THE CrOct CATALYZED REACTION OF AGE AND EHA[a]

	Temperature (°C)	Time	Reaction (%)	Stoichiometry
A. 0.1% catalyst level;[b] 5% AP[b]	25	1 day	13.8	1
	25	2 days	16.6	1
	25	3 days	26.3	1
	25	7 days	41.6	1
	25	10 days	48.6	1
	25	17 days	70.8	1
	50	6.5 hr.	13.8	1
	50	24.0 hr.	38.8	1
	50	5 days	77.7	1
	50	9 days	83.3	1
B. 1.0% catalyst level; 5% AP	25	5.5 hr.	25.0	1
	25	24.0 hr.	62.5	1
	25	48.0 hr.	80.5	1
	25	4 days	94.4	1
	25	7 days	100.0	1
	50	2.5 hr.	41.6	1
	50	5.0 hr.	62.0	1
	50	6.5 hr.	69.4	1
	50	24.0 hr.	97.2	1
	50	48.0 hr.	100.0	1

a/ Standard toluene stock solution.
b/ Weight percent based on weight of stock solution used.

45
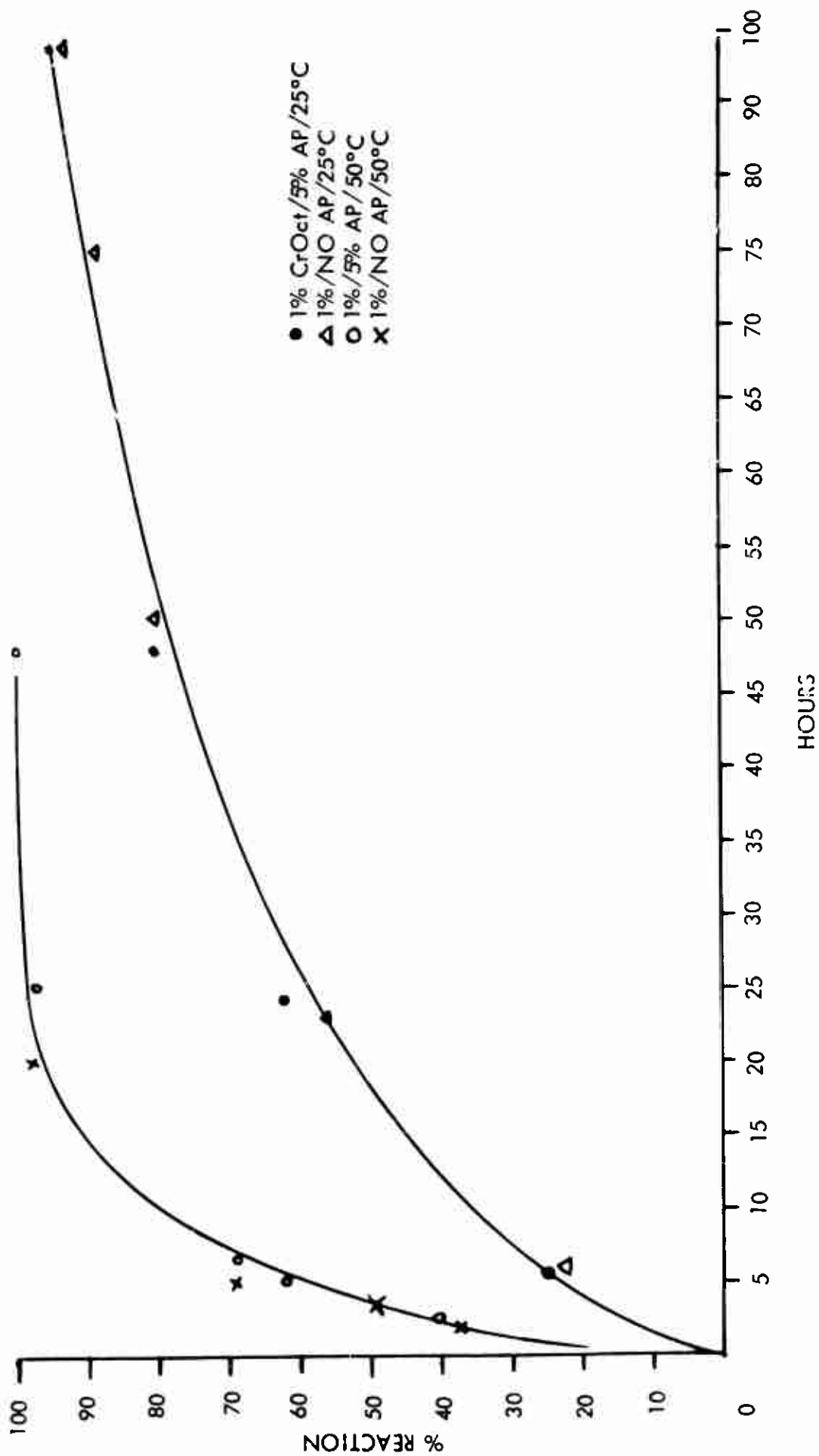
Figure 12 - Effect of Ammonium Perchlorate on the Rate of Reaction of AGE and EHA Catalyzed by CrOct

Legend:
- ● 1% CrOct/5% AP/25°C
- ▲ 1%/NO AP/25°C
- ○ 1%/5% AP/50°C
- ✕ 1%/NO AP/50°C

Y-axis: % REACTION
X-axis: HOURS

TABLE XIV

EXTRA-INGREDIENT COMPATIBILITY

Ingredient and Concentration Level (wt. % of total mixture)	End Use of Material	Catalyst and Concentration Level (wt. % of total mixture)	Time	Temperature (°C)	Percent Reaction
0.5% Roccal	surfactant	1% CrOct	15 min.	25	> 1
			24 hr.		65 7
			6 days		99 +
0.5% Roccal		1% Cr-neo-dec	5.5 hr.	25	> 1
			2 hr.		38.5
			days		77.1
			days		84.2
			days		85.7
0.5% phenyl-β-N	antioxidant	1% CrOct	7.5 hr.		41.4
			25.75 hr.	25	74.2
			6 days		99 +
			7 days		100
0.5% phenyl-β-N		1% Cr-neo-dec	5 hr.	25	11.4
			24 hr.		40.0
			4 days		82.9
			5 days		87.1
			6 days		90.0
			7 days		91.4
1% Al	fuel	1% CrOct	1 hr.	25	> 1
			25 hr.		68.5
			6 days		99 +
			7 days		100
1% Al		1% Cr-neo-dec	4 hr.	25	20.0
			26 hr.		35.7
			4 days		77.1
			5 days		84.3
			6 days		88.6
1% oxamid	ballistic modifier	1% CrOct	1 hr.	25	11.4
			24 hr.		65.1
			6 days		99 +
			7 days		99 +
1% oxamid		1% Cr-neo-dec	7 hr.	25	12.0
			24 hr.		32.9
			4 days		82.8
			5 days		84.3
			6 days		87.1
0.5% AO-2246	antioxidant	1% Cr-neo-dec	6.5 hr.	25	17.1
			24 hr.		54.2
			4 days		82.9
			5 days		90.0
			7 days		91.4
0.5% Fe₂O₃	ballistic modifier	No catalyst	33 days	25	> 1
		No catalyst	14 days	50	15.2
		No catalyst	33 days	50	19.4
1.0% Fe₂O₃		No catalyst	33 days	25	< 1
		No catalyst	14 days	50	9.7
		No catalyst	33 days	50	19.8
1.0% Fe₂O₃		1% CrOct	1 hr.	25	0
			3 hr.	25	12.2
			4 hr.	25	27.7
			5 hr.	25	41.6
			26 hr.	25	66.2
			4 days		99 +
			6 days	25	99 +
			33 days	25	100 mt: peaks

Figure 13 - The Effect of Selected Ingredients on the Rate of Reaction of EHA and AGE at 25°C Catalyzed by CrOct at the 1.0% by Weight Level

48
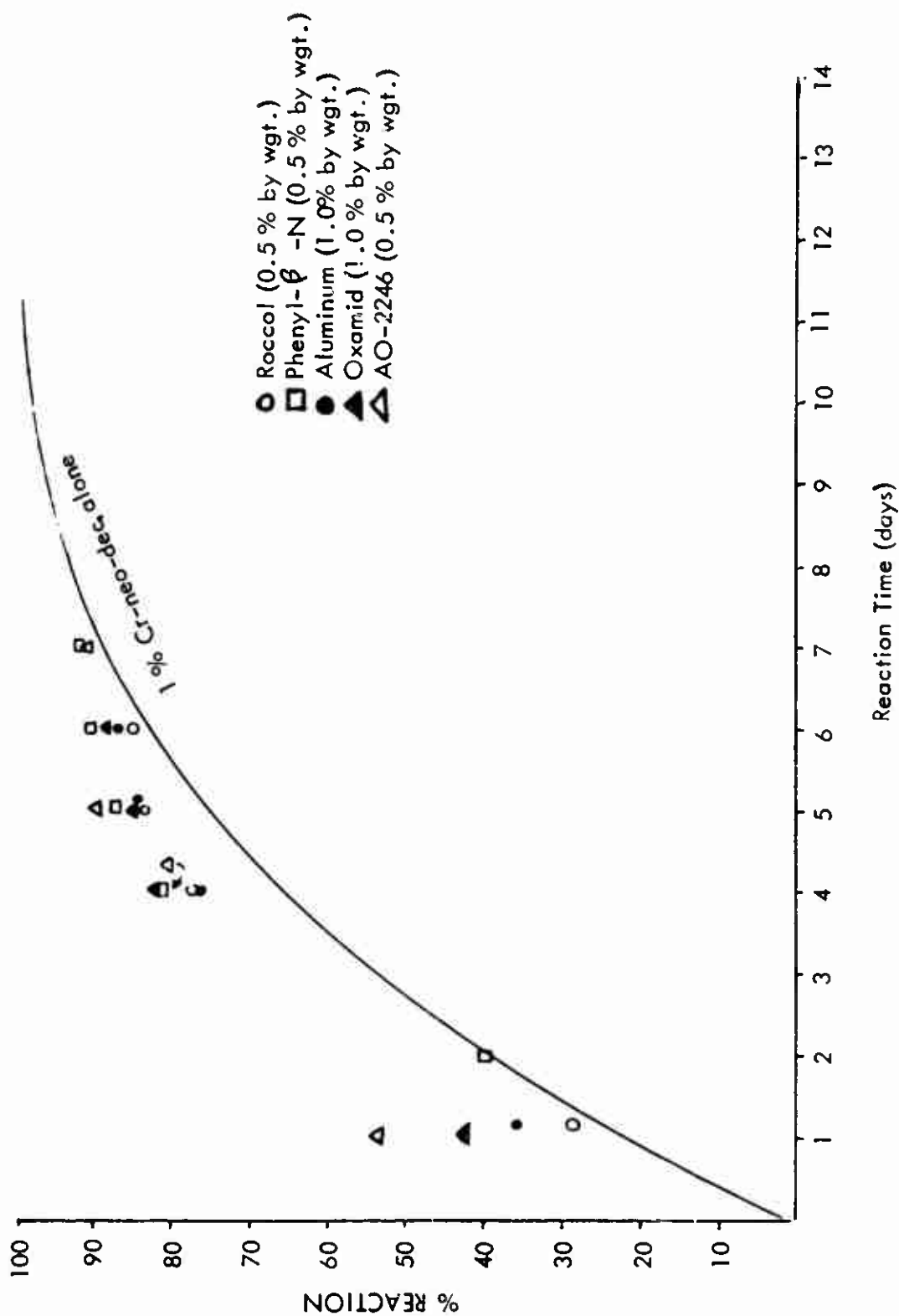
Figure 14 - The Effect of Selected Ingredients on the Rate of Reaction of EHA and AGE at 25°C Catalyzed by Cr-neo-decanoate at the 1.0% by Weight Level

However, even at these high concentration levels compared to the actual propellant situation, the antioxidants have no significant effect on the rate and direction of the cure reaction as compared to the effect of the catalyst itself.

The same can be said for the presence of aluminum, iron oxide, and oxamid; as expected, they have no intrinsic effect on the reaction (though iron oxide by itself at elevated temperatures and after extended time periods displays some slight catalysis for the reaction).

In Figure 14, the rate data are plotted for the Cr-neo-decanoate system. The acceleratory effect of the extra ingredient, once again, is minor but more pronounced than in the CrOct catalyzed reaction. This is not unexpected since Cr-neo-decanoate is a slower catalyst than the octoate (the neo-decanoate sample used here has roughly half the amount of chromium as the octoate) and, the extra contribution to the conversion rate by the other components is more noticeable.

B. Contaminants

The extra-ingredient compatability survey was extended to include the following potential contaminants: water, perchloric acid (which may be introduced by the oxidizer), nitric acid, ammonia, and n-propyl nitrate (as a model for nitrate ester).

1. Water: The effect of water on the model system is revealing in a mechanistic sense. Standard CrOct reaction systems (containing 0.01 mole of acid and epoxide) were contaminated with 9, 18, and 90 µl. of water. These water concentrations correspond to 0.0005, 0.001, and 0.005 mole of water, respectively. The rate data are listed in Table XIVa and plotted in Figure 15, relative to the rate profile for the reaction without added moisture. It can be seen that there is an initial rate enhancement corresponding to the amount of water present. The concentration effect diminishes in importance as the reaction proceeds, and water contamination does not significantly change the total time required for a complete reaction, nor does it alter the stoichiometry.

To provide a baseline for isolating the specific effect of water on the reaction, the behavior of the epoxide alone, and epoxide and catalyst with water, were examined. No reaction was detected between AGE and water after 10 days at 50°C. Very slight reaction was detected (less than 1%) under similar conditions when 1% CrOct was present in the system. Hence, water appears to act as a co-catalyst with CrOct in accelerating the acid epoxide condensation reaction.

50

TABLE XIVa

EFFECT OF WATER ON THE CrOct CATALYZED
REACTION OF AGE AND EHA[a]

Water Content (µl.)[b]	Temperature (°C)	Time (hr.)	Reaction[c] (%)
9	25	3.5	30.5
		24.0	66.6
		50.0	87.5
9	50	2.0	41.6
		5.0	75.3
		24.0	94.4
		48.0	99.0+
18	25	4.0	47.2
		26.0	62.5
		52.0	87.5
18	50	3.0	41.6
		5.0	61.1
		24.0	93.0
		48.0	99.0+
90	25	4.0	55.5
		26.0	66.0
		53.0	87.5
90	50	6.0	72.2
		25.0	93.0
		48.0	99.0+

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a/ Standard reaction system, 1% catalyst level.

b/ The test solutions contained 0.01 mole of reactants; 9 µl. of H_2O = 0.0005 mole, 18 µl. = 0.001 mole, 90 µl. = 0.005 mole.

c/ One trace product noted in GC with recorder at maximum sensitivity; major component in excess of 99% of product mixture.
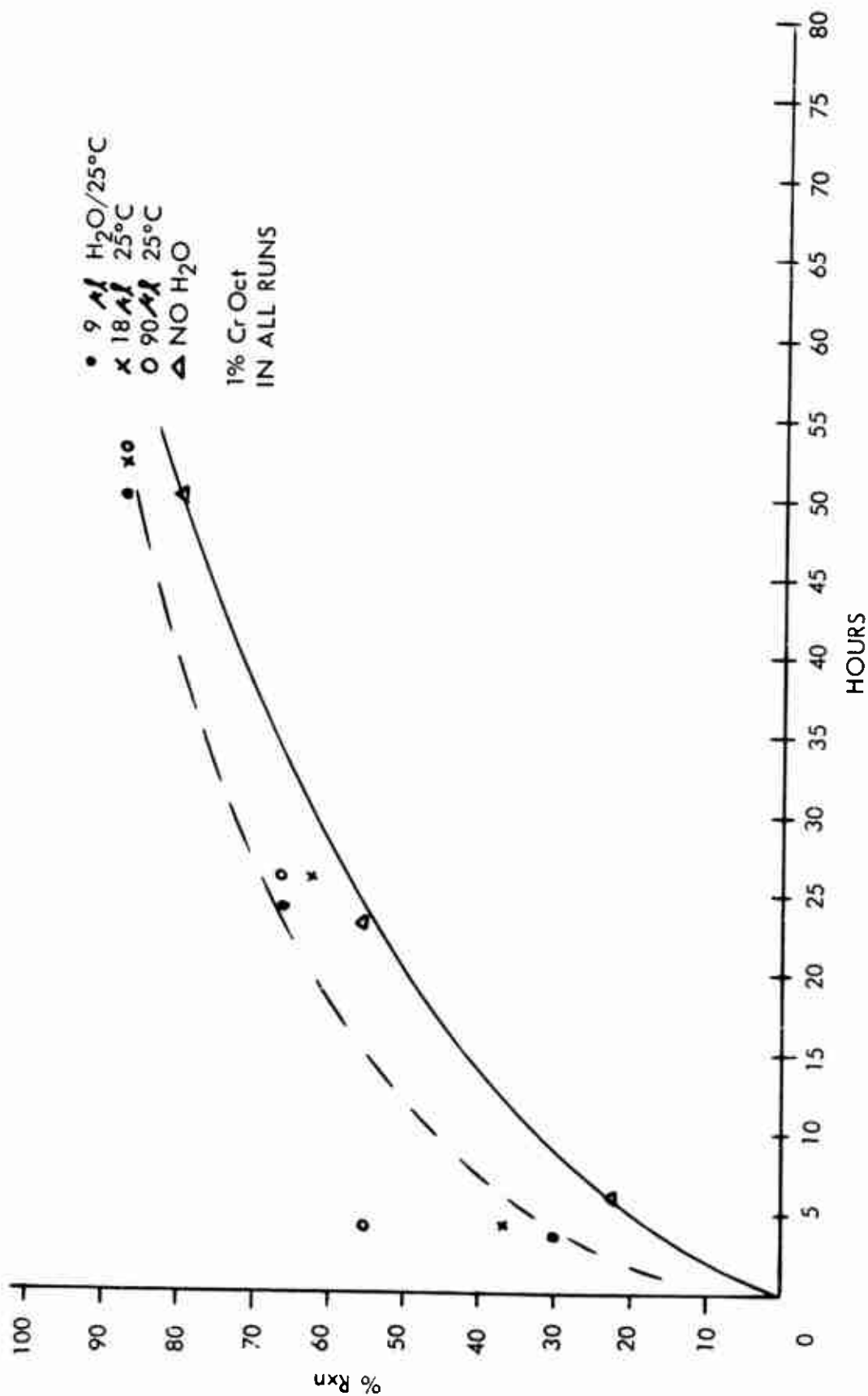
Figure 15 - Effect of Water on the Rate of CrOct Catalyzed Reaction of AGE and EHA

Summary:

System*					
AGE Mole	H$_2$O Mole	Catalyst (wt. %)	Temperature (°C)	Time (days)	Result
0.01	0.005	-	50	10	No reaction
0.01	0.005	1	50	10	1% loss of AGE; product detected

A trace product is formed at 50°C when water is added to a mixture of AGE and EHA without catalyst. The carboxylic acid is most likely acting as a protonic catalyst for glycol formation. The trace product has the same GC retention properties as that observed in the AGE/H$_2$O/CrOct system. Hence, water does act as a co-catalyst in the system for conversion of epoxide and carboxylic ester, and does not lead to significant side product formation. This effect is most pronounced during early stages of reaction when the ratio of catalyst to reactant is high.

The stoichiometry of the catalyzed AGE-EHA reaction in the presence of water is still excellent, though a second product, in trace quantity, has been detected with the GC recorder system at maximum sensitivity. This species has the same retention properties in the GC as those from the catalyzed AGE-H$_2$O reaction. (This material is most likely the glycol formed by opening the epoxide with water; i.e., HOCH$_2$CHOHCH$_2$OCH$_2$CH=CH$_2$.) It is concluded, therefore, that water has no practical effect on the stoichiometry of the condensation reaction. The effect of water on the components of the AGE/EHA/CrOct system is summarized in Table XV.

More significant, however, is the impact these observations have on the study of the mechanism of the reaction. The rate controlling step in the conversion sequence is obviously affected by the presence of water. Information from the literature and evidence from this study (discussed later) indicate the catalytic activation step involves interaction between catalyst and acid to give the carboxylate anion which, in turn, attacks the epoxide ring (Ref. 3). The presence of water would be expected to facilitate this ionization step. The chromium catalyst could be depicted as consisting of an inner sphere containing the primary metal-oxygen bond, and an outer sphere in which bonding forces would be weaker but still sufficient to hold solvent molecules or nucleophilic materials such as a carboxylic acid. This outer sphere may be the activation site; water

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* In toluene solvent.

TABLE XV

THE EFFECT OF H$_2$O ON THE COMPONENTS
OF THE EHA/AGE/CrOct SYSTEM

Reactants	Water Content (µL)	Temperature (°C)	Time (days)	Reaction (%)
AGE - no catalyst	9	50	6	NR
	9	50	12	NR
	9	50	26	NR
AGE + 1% CrOct	9	50	1	T
	9	50	6	T
	9	50	12	> 1
	9	50	16	> 1
	9	50	26	> 2
AGE/EHA - no catalyst	9	50	16	> 1
AGE/EHA - no catalyst	0	50	6	NR
Completed Reactions				
AGE/EHA/CrOct[a]	9	50	28	100 NC
	18	50	28	100 NC
	90	50	28	100 NC
	9	25	28	100 NC
	18	25	28	100 NC
	90	25	28	100 NC
Product - no catalyst	9	50	6	NC
	9	50	16	NC
	9	50	26	NC
Product + 1% CrOct	9	50	1	NC
	9	50	6	NC
	9	50	16	NC
	9	50	26	NC

NC = No Change.

NR = No Reaction.

a/ Surveillance.

present in the system would be bonded here (akin to solvation). The activation of the acid probably involves ionization to carboxylate anion by release of the proton. Water would facilitate this step. Mechanistically, the following steps are postulated.

$$-CO_2H + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[-CO_2{}^-MH^+\right]$$

$$\left[-CO_2{}^-MH^+\right] + \triangle \xrightarrow{k_3} -CO_2-CH_2-\overset{\overset{\displaystyle OH}{|}}{C}- \quad + M$$
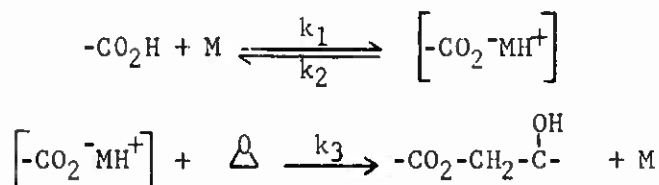
The effect of water on the rate of reaction in the model system was further explored using CrOleate and neo-decanoate as catalysts. Effects similar to those noted above for the octoate system were noted for the oleate and neo-decanoate catalyzed reactions as shown in Figures 16 and 17 respectively. Data tabulation is given in Tables XVI and XVII. Reaction is enhanced during initial stages, though not as sharply as in the CrOct case. The extent of initial rate enhancement appears to be independent of the actual amount of water present; this is unlike the CrOct situation. Since both Cr-neo-decanoate and CrOleate at the weight percent used have approximately half the amount of metal as compared to CrOct, the lowest water level (9 μl. or 0.0005 mole) may be beyond the critical interactant-ratio-point for the effect; that is, the CrOleate and neo-decanoate systems are "swamped" even at 9 μl. of water.

2. **Ammonia**: This material was introduced to the model cure system as ammonium hydroxide. The control experiment indicates reaction promotion by the base, especially at 50°C. The extent of catalysis at 25°C is insignificant relative to the normal rate promotion by CrOct. When both ammonium hydroxide and the Cr catalyst are present in the same system, the extent of reaction is significantly greater in a 24-hr. period than for the organometallic alone, i.e., 77.7% vs. 56%. The acceleration is due only partly to the amine, however, since the amount of water present in the system will increase the conversion in 24 hr. by ~ 10% over the Cr control rate. Side products were insignificant in quantity (two traces) indicating the ammonia to be catalyzing the desired esterification. (See Table XVIII.)

3. **HNO₃**: Nitric acid has no significant effect on the rate or stoichiometry of the catalyzed reaction and does not catalyze the main reaction itself. A slight yellowing of the control solutions was noted, especially at 50°C, but no product formation was noted at 25°C and ~ 5.0% at the elevated temperature. (See Table XVIII.)

4. **RCNO₂**: The nitrate ester functionality has no effect whatever on the rate or stoichiometry of the acid-epoxide reaction.

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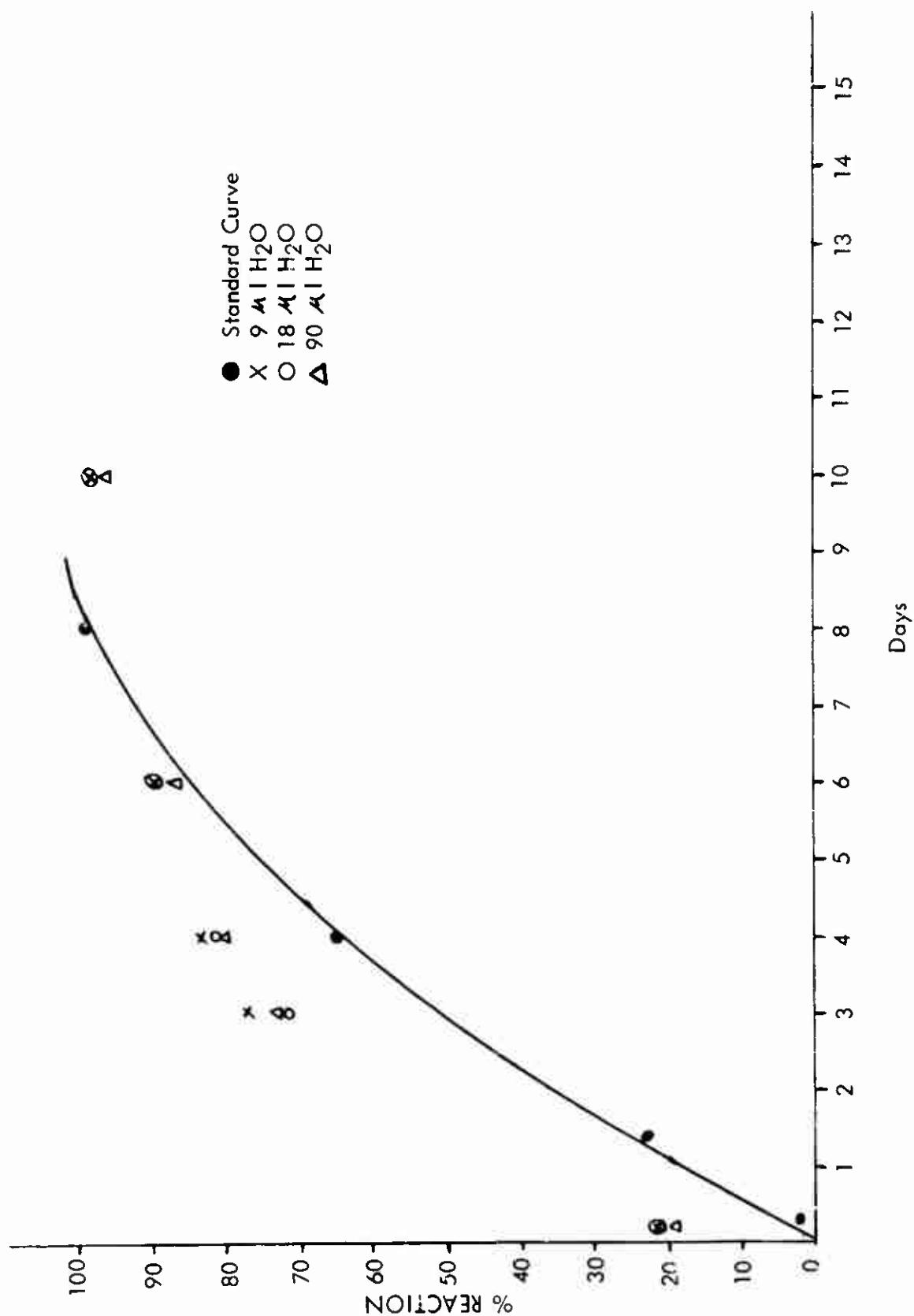
Figure 16 - The Effect of Water on the Rate of Reaction of AGE and EHA Catalyzed by CrOleate
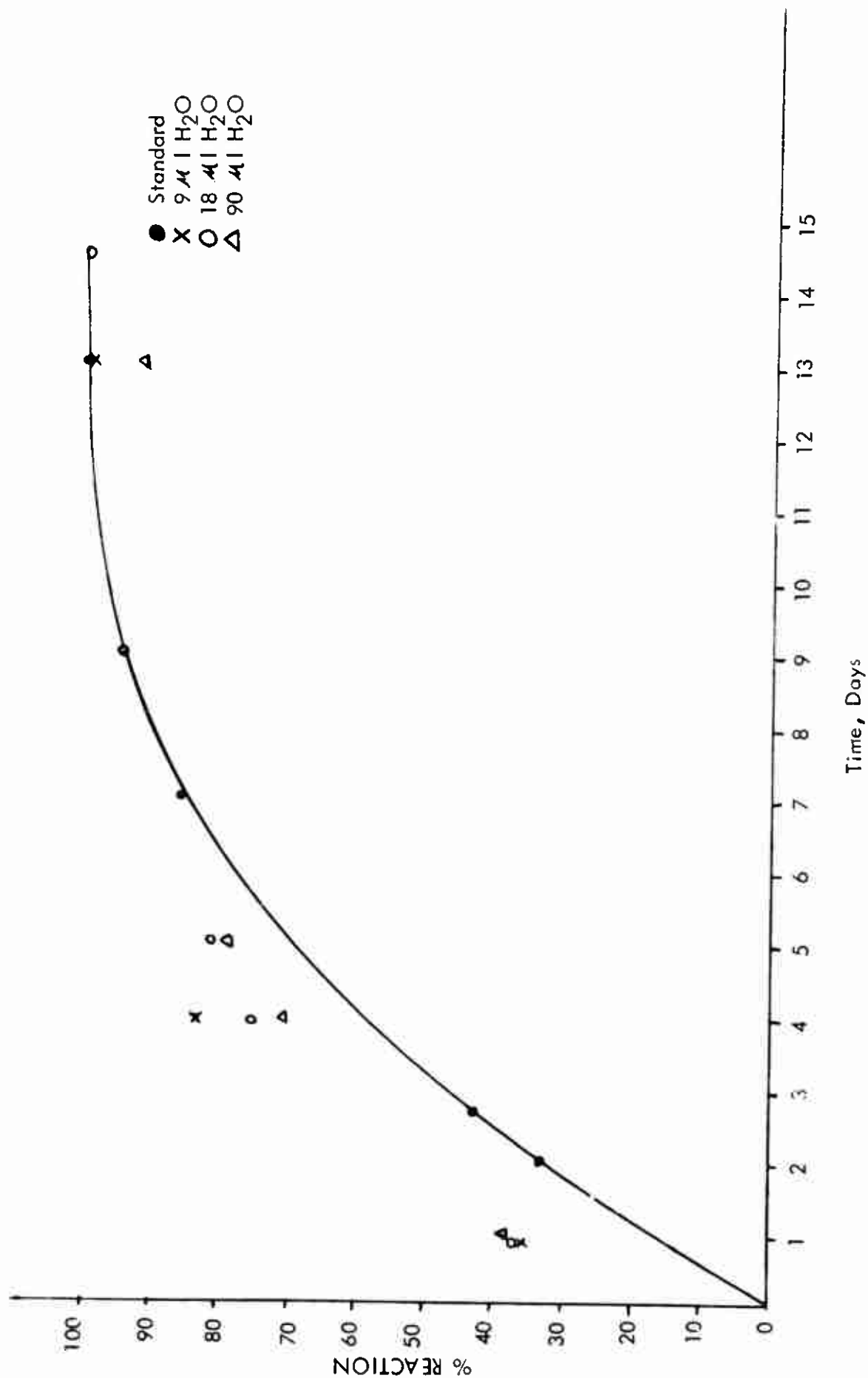
Figure 17 - The Effect of Water on the Rate of Reaction of AGE and EHA Catalyzed by Cr-neo-decanoate

57

TABLE XVI

EFFECT OF WATER ON THE REACTION OF AGE/EHA
CATALYZED BY CR-NEO-DECANOATE

Water Content (μL)	Temperature (°C)	Time	Reaction (%)
9	50	2 hr.	28.4
9	50	25 hr.	83.8
9	50	3 days	99+
9	50	18 days	100
18	50	3 hr.	22.9
18	50	25 hr.	83.8
18	50	3 days	99+
18	50	18 days	100
90	50	2 hr.	22.9
90	50	26 hr.	78.4
90	50	3 days	99+
90	50	18 days	100
9	25	22.5 hr.	35.2
9	25	90 hr.	83.8
9	25	13 days	99+
18	25	23 hr.	37.8
18	25	90 hr.	75.7
18	25	120 hr.	81.0
18	25	14 days	99+
90	25	24.5 hr.	37.8
90	25	91 hr.	70.3
90	25	120 hr.	78.4
90	25	13 days	91.8

TABLE XVII

THE EFFECT OF WATER ON THE REACTION OF AGE/EHA CATALYZED BY CROLEATE

Water Content (μL)	Temperature (°C)	Time	Reaction (%)
9	50	2 hr.	27.5
9	50	25 hr.	84.5
9	50	3 days	99+
9	50	18 days	100
18	50	3 hr.	24.2
18	50	25 hr.	85.0
18	50	3 days	99+
18	50	18 days	100
90	50	2 hr.	23.4
90	50	20 hr.	79.5
90	50	3 days	99+
90	50	18 days	100
9	25	7 hr.	21.5
9	25	3 days	77.2
9	25	4 days	83.5
9	25	6 days	89.9
9	25	18 days	100
18	25	7 hr.	21.4
18	25	3 days	71.2
18	25	4 days	81.5
18	25	6 days	89.7
18	25	18 days	100
90	25	7 hr.	19.1
90	25	3 days	73.4
90	25	4 days	80.6
90	25	6 days	86.5
90	25	10 days	97.2
90	25	18 days	100

TABLE XVIII

EFFECT OF SELECTED CONTAMINANTS ON THE CATALYZED REACTION OF AGE AND EHA

Contaminant	Catalyst Level (%)	Temperature (°C)	Time (days)	Percent Reaction
0	1	R.T.	24 hr.	56.0
H_2O a/	1	R.T.	24 hr.	65.0
HNO_3	1	R.T.	1	58.3
			4	96.1
			7	98.3
	0	R.T.	11	< 1
	1	50	1	97.2
			4	97.2
			7	99.1
	0	50	11	5.0
NH_4OH a/	1	R.T.	1	77.7
			4	91.6
			7	94.4
			11	97.5
	0	R.T.	1	5.5
			7	8.5
			11	16.6
	1	50	1	94.4
			4	99+
			7	100.0
	0	50	1	38.8
			4	52.7
			7	52.7
			11	63.8
$RONO_2$ a/	1	R.T.	1	58.7
			4	94.4
			7	100.0
	0	R.T.	11	0.0
	1	50	1	97.2
			4	99+
			7	100.0
	0	50	11	0.0
$HClO_4$ (9 µl. of 70% $HClO_4$)	1	R.T.	1	60.0
			4	94.0
			7	100.0
	0	R.T.	11	0.0 (trace product)
	1	50	11	< 2.0 (4 trace products)
	0	50	11	< 1.0 (4 trace products)

a/ Contaminant level was 0.1 to 1 molar ratio of contaminant to reactant (i.e., contaminant level actually exceeds catalyst amount).

60

5. Perchloric acid: As in the nitric acid case (in the concentration range studied) perchloric acid displayed no significant cure alteration effect in Cr system. A blank series was run first, i.e., reactants less catalyst employing three different concentration levels of the acid (9, 18, 90 µl. in the standard 5 cc. reaction sample). These amounts of acid would be representative of a catastrophic decomposition situation in the propellant. At both 25° and 50°C, four distinct products were observed in the gas chromatogram for the 18-µl. and 90-µl. samples, all in trace quantities. Only at 50°C and 90 µl. $HClO_4$ did the total amount of these products exceed 2% of the reactants. The nature of these reactions are speculative: oxidation, acid catalyzed condensation, and homopolymerization are possibilities. With 1% CrOct present in addition to the contaminants, reaction catalysis appeared normal at both 25° and 50°C at the two lower $HClO_4$ levels, with side reactions unchanged from the uncatalyzed systems. At the highest contaminant level, cure reactions occur, but numerous side reactions are noted by the gas chromatograph.

Conclusions possible at this point concerning the presence of $HClO_4$ in a formulation include: (1) trace levels of $HClO_4$ (that is, realistic levels) are not likely to affect catalytic effectiveness of the Cr catalyst (specifically CrOct); and (2) as expected, $HClO_4$ undergoes a number of reactions with organic material regardless of the presence of the catalysts, and in this sense will be detrimental to cure.

6. HF: HF (introduced as the aqueous solution) in an amount equivalent to a 1% loading of CrOct showed very definite epoxide consuming properties. In an uncatalyzed control, all epoxide was consumed at ambient temperature in 7 hr. EHA remained unaffected. The HF promoted reaction competes successfully with the CrOct catalyzed esterification reaction in terms of epoxide demand; only 44% of the total theoretical amount of product ester has formed when all epoxide has been consumed. The gas chromatograph indicates four side products due to HF promotion. A different effect, discussed below, was observed by ABL in propellant systems. (See Table XIX.)

7. N_2O: N_2O showed no catalytic properties in the uncatalyzed control and its presence did not alter the rate and stoichiometry of the CrOct promoted reaction.

C. Amine Catalysis Studies

Since many propellant additives, e.g., processing acids and antioxidants, are amines or amine salts, an examination of their potential catalytic properties in the acid-epoxide system was undertaken. The objective of this study was to identify amine types which would interact with the cure functionalities to the detriment of the main reaction; in a quantitative sense, reaction rates (e.g., epoxide consumption) relative to the main reaction were determined.

61

TABLE XIX

EFFECT OF HF ON EPOXIDE-ACID REACTION[a]

Catalyst	Time (hr.)	% Epoxide Consumed	% Acid Consumed
0	5	97.0	0.0
	25	100.0	0.0
1% CrOct	5	27.9	5.0
	25	30.8	7.0
	8 days	100.0	44.1

[a] HF amount equivalent to 1% CrOct loading.

Two Lewis bases, pyridine and triethylamine, were selected to provide points of comparison between amine catalysis and organometallic catalysis of the acid-epoxide reaction. The results are shown in Table XX; even at 50°C the amines are significantly less effective than Cr salts as catalysts for the solution epoxide-acid reaction. The results reported above for ammonia also agree with this conclusion.

TABLE XX

AMINE CATALYSIS STUDIES OF EHA/ACE MODEL SYSTEM AT 50°C[a]

Time	% Reaction		
	Pyridine[b]	Triethylamine[b]	CrOct
2 hr.	< 1	< 1	50
22 hr.	2.5	< 1	98
4 days	30.7	7.7	100
7 days	34.6	23.1	
19 days	66.6	76.9	
27 days	66.6[c]	76.9[c]	

a/ Standard model reaction system used.

b/ Amounts of amine catalyst used were equal on a molar basis to a 1% loading of CrOct, i.e., 9×10^{-5} moles, or 0.0073 g. pyridine and 0.0093 g. triethylamine.

c/ Stoichiometry of 0.99 noted; one trace side product detected.

An interesting problem arose during propellant formulation studies at ABL: a number of mixes containing the antioxidant TDPA (thiodiphenylamine) did not cure. Mix viscosity increased significantly and no cure was achieved--an unusual occurrence since TDPA has been used successfully in numerous similar ABL propellants cured at 140°F. To determine whether the effect is due to a chemical interaction, the series of experiments was undertaken; those in model systems are listed in Table XXI.

TABLE XXI

MODEL SYSTEM STUDIES

Reactant Combination	TDPA % by Wt.	CrOct % by Wt.	Temperature	Observation
EHA/AGE	0.5	0.0	R.T.	No reaction or
	0.5	0.0	50	change in 7 days
EHA/AGE	1.0	0.0	R.T.	
	1.0	0.0	50	
EHA/AGE	2.0	0.0	R.T.	
	2.0	0.0	50	
EHA/AGE	1.0	1.0	R.T.	Normal rate and
	1.0	1.0	50	stoichiometry behavior

No adverse or unexpected effect due to TDPA was noted in the model studies. The uncatalyzed solution studies at both R.T. and 50°C showed the typical amine effect--only a slight product formation (trace amount, less than 1%) in the presence of the antioxidant after a duration of at least 7 days. With CrOct present along with TDPA, the normal catalyzed reaction behavior is observed for EHA/AGE at both R.T. and 50°C.

Reaction behavior was examined in the polymer system and the results from those experiments are given in pages 77-79.

D. Summary of Contaminant and Extra-Ingredient Effects

No evidence has been found of catalyst poisoning in the Cr system by common propellant ingredients and contaminants. Oxidizing acids such as HNO_3 and $HClO_4$ (at realistic contaminant levels) do introduce trace amounts of side products; however, these side reactions are insignificant in a rate and stoichiometric sense, when compared to the course of the main esterification reaction. Amines are co-catalysts for the esterification reaction but, again, they are poor at ambient temperature compared to CrOct. The presence of an amount of amine in a system equimolar to the Cr catalyst will result in an acceleration of the conversion rate during earlier reaction stages equal to no more than 10% of the Cr rate. The presence of water in the system causes a similar rate effect in the model systems, though in the binder situation this rate acceleration effect is not as noticeable.

V.

CATALYST EVALUATION IN BINDER SYSTEM

Following the selection of candidate catalysts from the model studies, the evaluation was expanded to actual polymer systems. The purpose of this work was: (1) to correlate the results of the model system studies with the actual binder situation; (2) to relate catalytically controlled chemical conversion behavior to physical effects, such as gelation, pot life, catalyst levels, total cure time, etc.; (3) to study effects that could not be determined by GC, for example, to examine the effects of high molecular weight materials such as plasticizers and surfactants on the outcome of the catalyzed cure reaction. Infrared spectroscopy was applied to the problem of following the conversion of Telagen CT to ester by observing the decrease in absorption at 5.9 µ (carbonyl stretching frequency for acid) and the increase in the peaks at 5.8 µ (carbonyl stretching frequency for ester) and 2.9 µ (OH stretching vibration) (Refs. 3 to 5).

A description of the experimental method is given in the experimental section along with a discussion of the advantages and disadvantages of the procedure.

Quantitative determinations are made by reference to an empirical absorbance ratio-concentration curve. In some case, where only relative comparisons were desired of general reaction trends, the data are presented as plots of absorbancy versus time.

A. Binder Cure Behavior in Cr Salt Catalyzed Systems

It was desired to determine the effect of free (residual) acid in the catalyst on the overall trend of the reaction. Figure 18 shows a comparison of the rates of reaction for Telagen CT and AGE catalyzed by CrOct and CrOleate. The quantities of active ingredient, Cr, are the same for both reactions; 2-ethyl hexanoic acid was added to the 10.5% CrOct to compensate in kind for the additional oleic acid present in the 4.2% CrOleate. The patterns for both reactions are very similar, though the octoate catalyzed reaction appears to proceed faster initially to a rate plateau, while the oleate goes farther toward completion in the same time period. This difference in rates is most likely due to differences in solubility between the CrOct and CrOleate; the oleate is more soluble in organic materials than the octoate. The addition of the compensatory acid to the CrOct does not appear to change the reaction pattern or rate of reaction relative to the same catalyst without the free acid (10.5% CrOct) as long as the same amount of active metal is used.

65
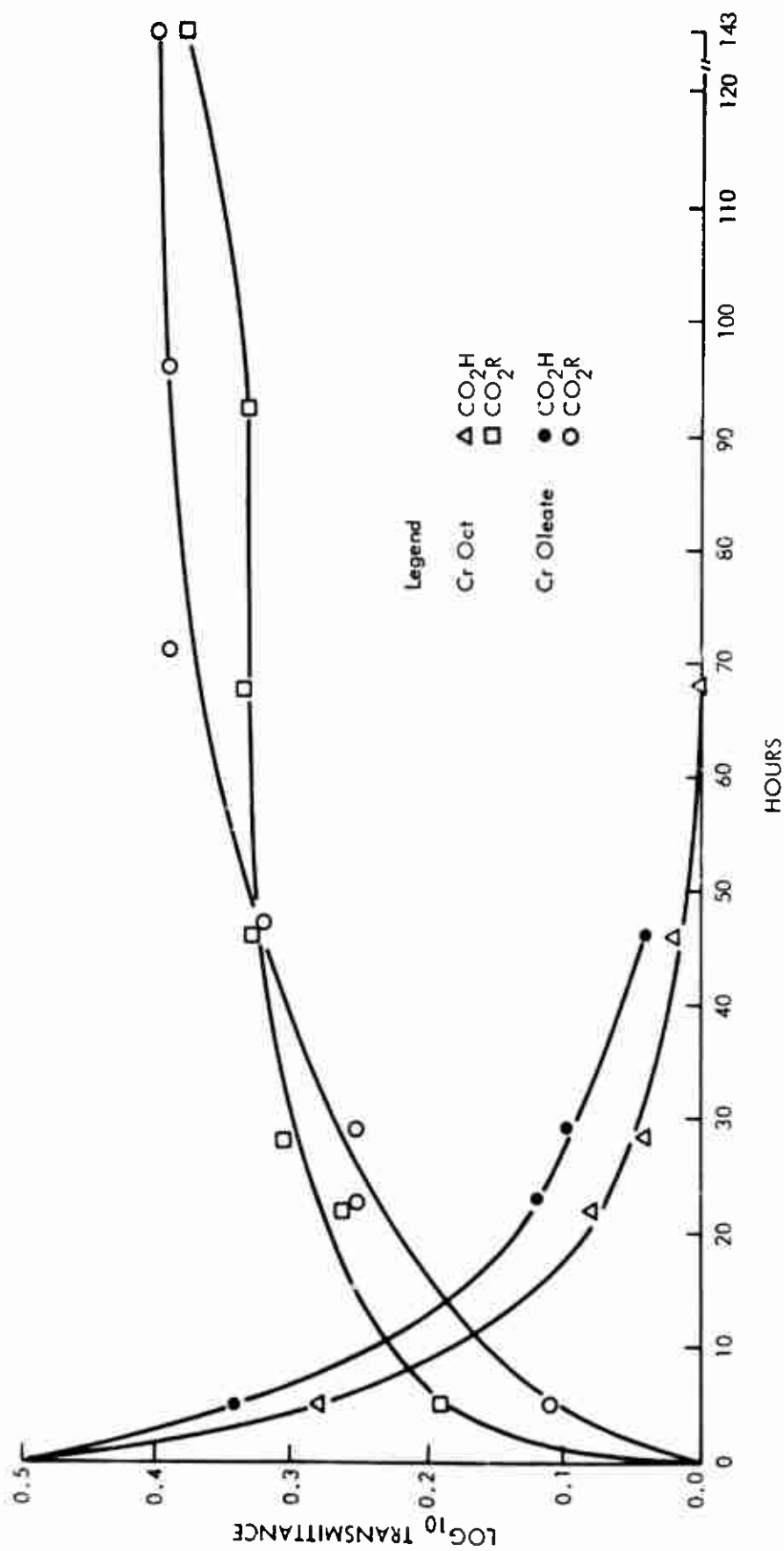
Figure 18 - Comparison of Rates of Reaction for Telagen CT/ACE Catalyzed by CrOct and Cr Oleate, Respectively

The conversion profile for the reaction of Telagen CT and ERLA 0510 catalyzed by CrOct at the 1% by weight level is given in Figure 19. Reaction is about 75% complete in 5 hr. The rates of disappearance of acid and appearance of alcohol and ester are equal during this stage. Beyond this point acid is consumed at a faster rate (i.e., loss of abosrbance at 5.9 µ) than either ester or alcohol is formed. At 100 hr., the amount of acid consumed equals the amount of ester formed. This pattern is experimentally reproducible, hence it is a real effect and not due to error in the method. The alcohol present after 100 hr. is about 5% less than theoretical, the difference in this case is the method. The rapid decrease in acid can be explained in terms of a shift in kinetics and the resulting survival of metal-coordinated carboxylate. After approximately 75% reaction, diffusion of reactants is extremely slow. Diffusion of the catalyst will be faster than epoxide since, at this stage, the latter being polyfunctional will have its mobility significantly reduced through incorporation of one or more of its epoxides into the fixed binder matrix. Therefore, catalyst diffusion and coordination with carboxyl will be rapid compared to the condensation, and this catalytic intermediate will exist as such for a longer time period. Hence, there will be a difference in the rates of disappearance of carboxylic acid and appearance of ester. This point will be dealt with in more detail below.

Of significance in a processing sense, 1.0% loading of CrOct leads to 75% conversion in 5 hr. This may be too fast for good pot life characteristics. Studies were therefore undertaken using 0.2, 0.4, and 0.8% loadings of CrOct. Figure 20 shows the results of this experimental series in terms of the rate profile (conversion of carboxylic acid) for the cure of Telagen CT with ERLA 0510. At the 0.8% catalyst level the rate transition point (discussed below in terms of gelation) appears to begin at around 6 hr., while with 0.4% catalyst inflection point on the curve occurred at 20 hr. The rate of disappearance of COOH for the reaction catalyzed by 0.2 and 0.1% CrOct, respectively, do not display any sharp shift in the time range of the experiment, a point in agreement with 30 g. propellant mix studies (discussed later). The minimum catalyst level for cure in a reasonable time period appears in the 0.4% range; results from ABL propellant processing studies indicate that this range is indeed 0.37 to 0.4% catalyst level.

Figure 21 displays the decrease in acid carbonyl content with time for an equivalent mixture of Telagen CT and CrOct. This plot is a demonstration of the "precoordination" effect; as the amount of carboxylic acid decreases relative to the amount of catalyst present, the more pronounced is the effect. Hence, it is reasonable to propose that the deviation in the rate of disappearance of acid and appearance of ester noted in the above studies is due to coordination of unreacted acid with catalyst.
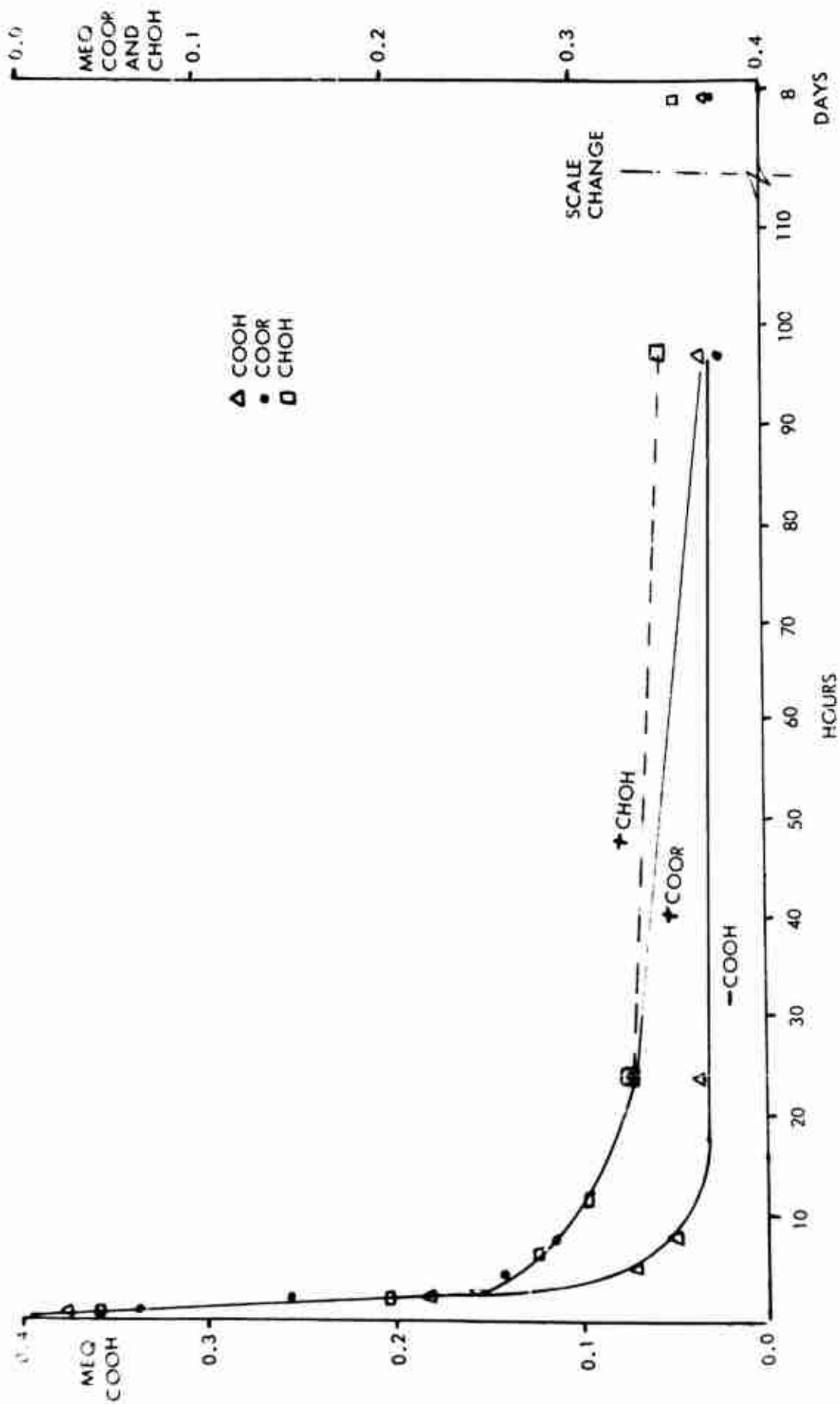
Figure 19 – Reaction Profile for the CrOct Catalyzed Cure of Telagen CT with ERLA 0510 (CrOct at 1% by weight level)
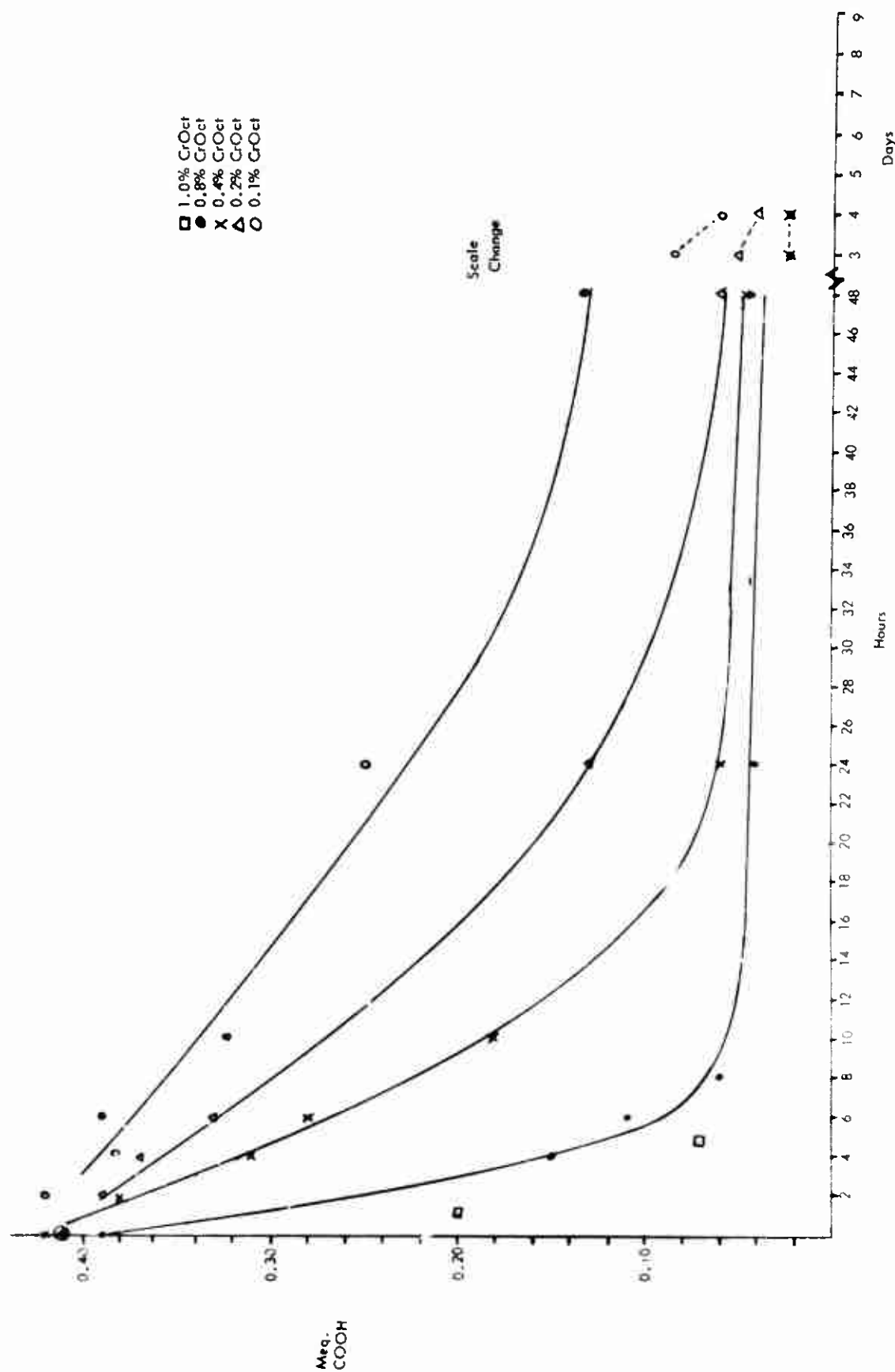
Figure 20 - The Effect of Catalyst Quantity on the Rate of Cure of Telagen CT with ERLA 0510 (decrease in acid)
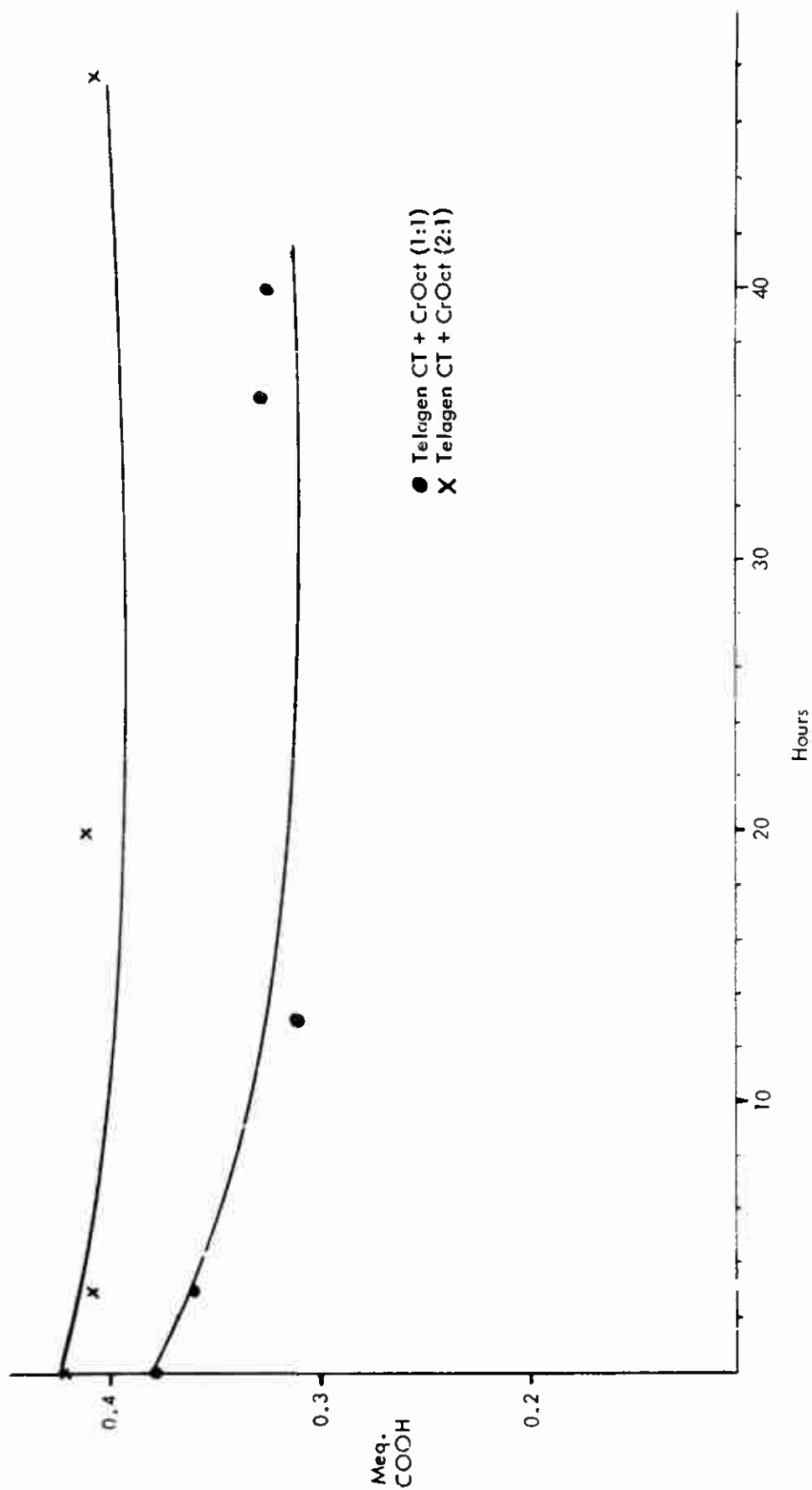
Figure 21 - The Interaction of Telagen CT Carboxylic Acid Group with CrOct

At this point some comment should be made concerning the reasons for the character of the reaction conversion curves. In general, the chemical reaction behavior of polymers is essentially the same as that for low molecular species with the exception of systems in which diffusion rates are low (Refs. 5 and 6). Where gelation occurs, reaction continues only slightly beyond the gel point and a complete reaction does not occur. French and co-workers (Ref. 5) have demonstrated that the maximum extent of polymer reactions is dependent on functionality and suggest that the limiting factor in determining the final extent of reaction depends on the geometry of the solid matrix formed by the cure reaction (functionality dependence) and not on thermodynamics or kinetics.

This effect becomes apparent when results from the model system studies are compared with those from the binder reactions. The solution reactions go to completion, while the polymer binder cure reaction consumes only 75 to 90% of the starting materials. Based on the French hypothesis, then, the extent of reaction (but not rate) is not controlled by the catalyst and is a function only of prepolymer and curative structure. Time to gelation and rate of increase in binder viscosity during cure are catalyst dependent. Since these parameters are of critical importance to processing, catalyst selection is crucial to the success of that procedure. In simplest terms, gelation occurs when cure linkage (especially cross-linking) formation has reached a point where a sufficient number of cross-links exist to give a three-dimensional matrix with mechanical integrity (i.e., solidification occurs). Reaction of the remaining cure functionalities becomes increasingly dependent on diffusion and the rate of ester formation will be curtailed sharply. Referring to Figure 19, Point A is most likely the beginning of the gelation process and Point B may be the gel point (this cannot be established without direct correlation with actual gel point determination studies). A-C represents the "precoordination" range for unreacted carboxylic acid groups with the catalyst--the only truly diffusable species present in the system at this point.

The effect of other binder parameters (e.g., mixed curative, plasticizer) were investigated in the Telagen CT system at both 1.0 and 0.4% CrOct levels as shown in Table XXII and Figure 22. At the 1% CrOct level, the reaction rate profiles are identical regardless of the nature of the curative (all tri-epoxide vs. an equivalent mixture of di- and tri-epoxide) or the presence of plasticizer. When 0.4% CrOct is used to catalyze the reaction of the mixed epoxide and Telagen CT, the presence of plasticizer does not alter the conversion pattern. There appears to be a slight increase in the rate of conversion for the mixed curative system compared to the all tri-epoxide (though the differences in values are precariously close to the experimental error of the method).

71

TABLE XXII

PARAMETER STUDY FOR AMBIENT CURE OF TELAGEN CT

Curative (meg. ratio)	Catalyst Level (wt. + % CrOct)	Plasticizer Level (wt. + % polybutene)	Time (hr.)	% Reaction
DER 332 (0.5) + ERLA 0510 (0.5)	1.0	5.0	1	3.0
			2	57.5
			4	74.2
			10	85.0
			24	85.0
			48	87.8
			14 days	89.0
DER 332 (0.5) + ERLA 0510 (0.5)	0.4	5.0	2	30.3
			4	39.3
			10	66.6
			24	82.0
			48	82.0
			4 days	89.0
			14 days	89.0
DER 332 (0.5) + ERLA 0510 (0.5)	1.0	0.0	1	16.6
			2	54.5
			4	72.7
			10	83.3
			24	85.0
			48	85.0
			14 days	90.1
DER 332 (0.5) + ERLA 0510 (0.5)	0.4	0.0	1	9.0
			2	22.7
			4	36.4
			10	56.1
			24	72.7
			48	84.8
			8 days	85.0
			14 days	90.0
ERLA 0510 (1.0)	1.0	5.0	1	12.7
			2	57.6
			4	76.0
			10	81.8
			24	85.0
			48	85.0
			8 days	85.0
			14 days	88.0
ERLA 0510 (1.0)	0.4	5.0	1	13.6
			2	39.4
			4	47.0
			10	63.6
			24	82.0
			48	83.3
			8 days	87.0
			14 days	89.0

Figure 22 - Comparative Cure Rate Behavior of Telagen CT Binder Containing Mixed Curative and Plasticizer (percent reaction - decrease in COOH concentration)

73

An interesting observation was made when the effect of plasticization on the rate of cure of Telagen CT with all tri-epoxide curative was studied. Figure 22 shows a comparison of rate patterns for plasticized reactions at both 1.0% and 0.4% catalyst levels. No effect is noted at the 1% level; while the 0.4% CrOct reaction is accelerated by the presence of plasticizer during early stages of cure (up to approximately 70% conversion) compared to the unplasticized case.

Several propellant components, listed in Table XXIII, were added to Telagen-ERLA mixtures to determine whether their presence would alter the CrOct catalyzed cure reaction. The data are plotted in Figure 23 relative to the rate data for the binder mixture without the ingredients. At the 1% catalyst level, AP and water had no effect on the rate of the cure reaction. The presence of lecithin or Fe_2O_3 tends to slow the reaction during early stages of cure, though the total time to 90% conversion is unaffected. At this writing, the 0.4% catalyst level studies of the lecithin and Fe_2O_3 effects are under way. At the 0.4% catalyst level, again, AP and water do not alter the rate behavior of the cure reaction.

The binder cure rate studies reported above employ an equivalent mixture of carboxylic acid and epoxide. Since E/C* ratios other than one are often employed in formulation, the effect of this parameter was studied in the Telagen CT/ERLA 0510 system. Table XXIV summarizes this experiment.

Excess epoxide gives a higher cure rate than in the analogous excess Telagen system. Cure is complete in a shorter time period (2 days vs. 7 days). The final reaction segment is much shorter than in the excess Telagen situation. Ultimate reaction is slightly higher, approximately 4%, in the excess epoxide system.

In summary, the ambient temperature cure behavior of carboxylic acid prepolymer with epoxide remains essentially unaffected by the presence of binder and propellant components. i.e., the total cure times appear unchanged. Diffusion of reactants and catalyst is a rate controlling parameter as evidenced by the differences in rate observed between di- and tri-epoxide curatives, and in the presence of plasticizer. These observations are in agreement with the hypothesis made above concerning chemical conversion behavior and its relation to physical effects.

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* E/C - epoxide/carboxyl equivalence ratio.

TABLE XXIII

EXTRA-INGREDIENT EFFECTS ON AMBIENT CURE OF TELAGEN CT WITH ERLA 0510 CATALYZED BY CrOct

Ingredient (% by wt.)	Catalyst Level (% by wt.)	Time (hr.)	Reaction (%)
AP (5.0)	1.0	1	28.8
		2	60.6
		4	72.7
		11	81.8
		24	83.3
		48	84.0
		8 days	90.0
AP (5.0)	0.4	2	18.1
		4	31.8
		11	56.0
		24	78.7
		48	81.8
		5 days	85.0
		8 days	86.0
H_2O (0.04 meq.)	1.0	1	27.2
		2	50.0
		4	68.1
		11	81.8
		24	82.0
		5 days	86.3
H_2O (0.04 meq.)	0.4	1	13.6
		2	21.2
		4	33.3
		11	66.6
		24	78.7
		48	82.0
		5 days	88.0
Lecithin (0.5)	1.0	2	31.8
		4	51.5
		11	75.7
		24	78.7
		48	81.8
		5 days	83.0
Fe_2O_3 (1.0)	1.0	2	27.3
		4	46.9
		11	75.8
		24	78.8
		48	81.0
		5 days	84.0

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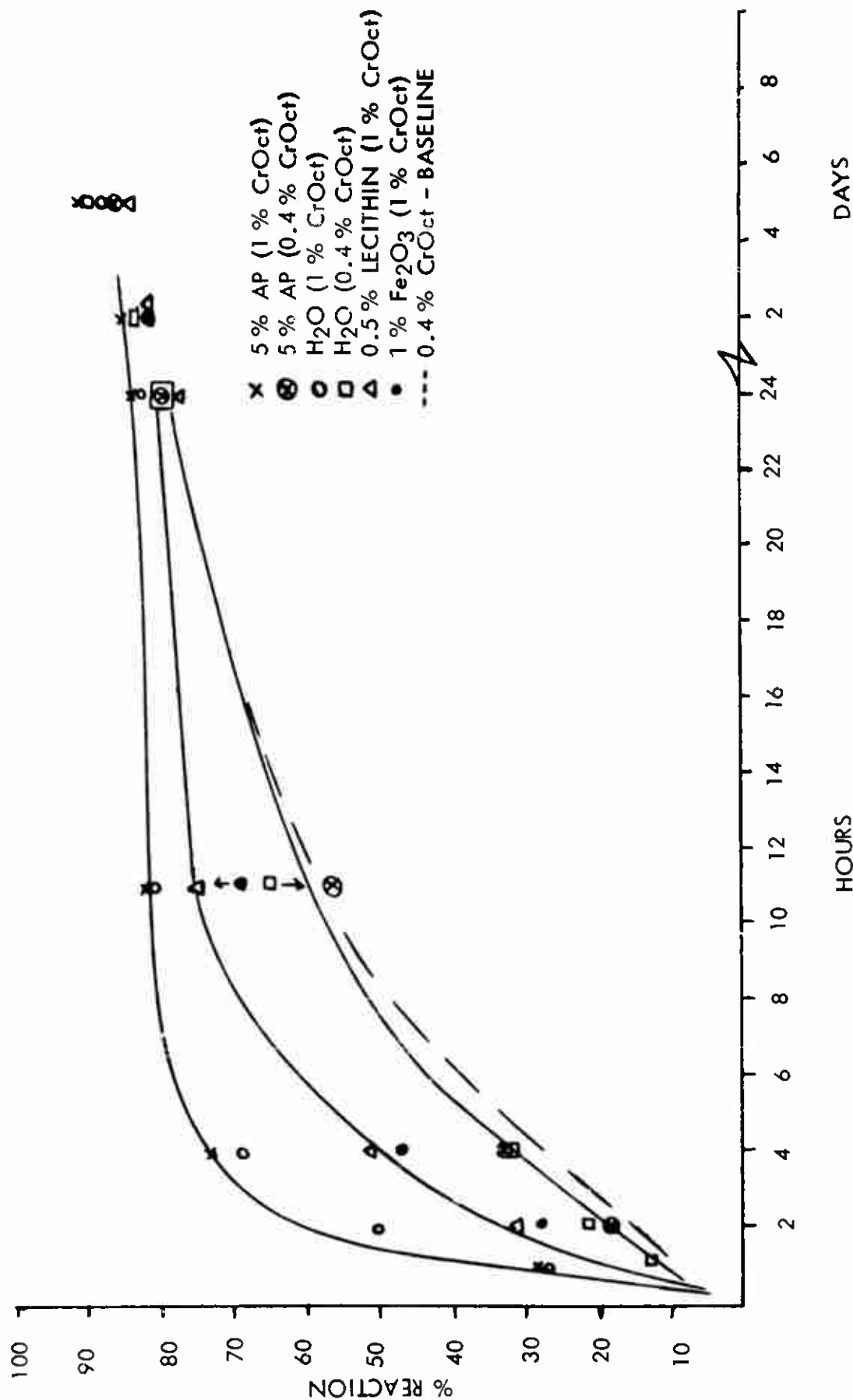
Figure 23 - Extra-Ingredient Effects on Rate of Cure of Telagen CT with ERLA 0510 at 1.0 and 0.4% CrOct Levels (percent reaction in terms of decrease in COOH)

Legend:
- ✕ 5% AP (1 % CrOct)
- ⊗ 5% AP (0.4% CrOct)
- ◐ H₂O (1 % CrOct)
- □ H₂O (0.4% CrOct)
- ◁ 0.5% LECITHIN (1 % CrOct)
- ● 1 % Fe₂O₃ (1 % CrOct)
- --- 0.4 % CrOct - BASELINE

TABLE XXIV

EFFECT OF VARYING E/C RATIO ON CURE REACTION

Telagen/ERLA 0510	Temperature (°C)	Time (hr.)	% Rxn
1/0.75	25	2	26.4
		10	51.9
		23	59.0
		48	61.2
		3 days	62.7
		7 days	64.6 - cured
		10 days	64.6
0.75/1	25	2	22.0
		10	59.3
		23	68.3
		48	68.6 - cured
		3 days	68.6

B. Cure Processing Problem - TDPA

In the propellant formulation phase of the program, ABL encountered processing difficulty when the antioxidant TDPA was incorporated in certain mixes. The studies described below were an attempt to isolate and identify the components which were interacting to produce the effect.

Results for gumstock and filled binder cure studies are shown in Table XXV.

The Telagen CT-ERLA 0510 gumstocks with 0.4 and 0.5% CrOct and 1% TDPA showed normal reaction behavior relative to the reaction profile at these catalysts levels without the antioxidant. Hence, TDPA does not appear to interfere directly with either of the reactants or the action of the catalyst on the cure functionalities.

The addition of AP to the gumstock mixture does not change the cure behavior. The samples loaded with 50% AP and 20% Al also appeared to cure completely in approximately 10 days (the observations in this case are only qualitative since no measurement of cure was made other than visual and handling observations).

A closer examination was made of the possibility of interaction of TDPA antioxidant with the specific curative ERLA-0510 (previous quantitative work had been done in the model test solution). Epoxide consumption in TDPA/ERLA-0510 mixtures was measured by titration of the epoxide.

77

TABLE XXV

TDPA BEHAVIOR IN BINDER

Binder Composition % by Wt. of Binder	Solids Loading % by Wt. of Total	Temperature	Observation
Telagen CT/ERLA 0510/0.5% CrOct/1% TDPA	0	R.T.	Normal rate and cure behavior
Telagen CT/ERLA 0510/0.4% CrOct/1% TDPA	0	R.T.	
Telagen CT/ERLA 0510/0.5% CrOct/1% TDPA	63	R.T.	
Telagen CT/ERLA 0510/0.4% CrOct/1% TDPA	63	R.T.	
Telagen CT/ERLA 0510/0.5% CrOct/1% TDPA	50-AP 20-Al	R.T.	
Telagen CT/ERLA 0510/0.4% CrOct/1% TDPA	50-AP 20-Al	R.T.	

Table XXVI shows a summary of the results of the experimental runs.

TABLE XXVI

EPOXIDE DEMAND-ERLA-0510 (LOT 11)

System	TDPA Level Wt. % Based on Curative	Temp. (°C)	Time (hr.)	Epoxide Analysis (meq/sample)	Comment
1. ERLA-0510 Baseline	0	25	0	11.33 ± 0.20	Based on 8 determinations
2. ERLA-0510/ TDPA in Chloroform Soln.	10	25	24	11.29	No change
	1	25	24	11.19	No change
	0.5	25	24	11.56	No change
	1	50	24	11.19	No change
3. ERLA-0510/ TDPA Neat Mixture	10	25	5 days	10.11	10.7% consumption
	1	25	5 days	11.09	~ 1% Rxn
	0.5	25	5 days	11.01	~ 1% Rxn

78

As the weight ratio of TDPA to curative increases, there is an increased epoxide demand in the system. This conclusion appears to hold true only in the bulk (neat) mixture situation and not in solution. In addition, these observations agree with the propellant cure data from ABL. The nature of the epoxide consumption is most likely a homopolymerization reaction; such an occurrence would explain the increase in viscosity and concomitant decrease in cure rate (homopolymerization of a polyfunctional material such as ERLA-0510 would undoubtedly lead to significant viscosity increases). To complicate matters further, samples from a new lot of ERLA 0510 do not exhibit the consumption behavior in the presence of TDPA as noted of the previous lot. These data showing no epoxide loss are summarized in Table XXVII.

TABLE XXVII

EPOXIDE DEMAND BY TDPA AT 25°C
(ERLA 0510 Lot 9)

Time	Milliequivalents Epoxide Remaining (ERLA-0510) Sample			
Days	25% TDPA[a]	12.5% TDPA	10% TDPA	5% TDPA
0	11.50 ± 4	12.50	12.60	13.20
1	11.50	12.30	12.42	13.14
4	11.91	12.30	12.53	13.00
7	11.17	12.51	12.34	13.04
15	11.63	12.04	12.36	13.48

a/ Wt. % TDPA of total sample (TDPA + ERLA 0510).

Conclusions are as follows: (1) TDPA does not appear to interact with the carboxylic acid or epoxide groups to any appreciable extent for a length of time equal to the duration of the processing period; (2) TDPA does not interfere with the activity or CrOct as a catalyst for the epoxide-acid condensation reaction in either the model or binder situation; (3) the presence of AP at a moderately high loading (63%) does not alter the above conclusions; (4) aluminum in the formulation containing TDPA does not alter the cure behavior of the system. The problem may be unique to the lot of ERLA used in the propellant formulation study.*

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* A sample from this lot homopolymerized during storage for no apparent reason.

C. Evaluation of CrDIPS System

CrDIPS* is a catalyst system recommended for the all-epoxide cure of CT binders by the Explosives Research and Development Establishment, Waltham Abbey, England. The sample used in this study was supplied by AFRPL. Compositional data and a recommended formulation follow:

Catalyst: CrDIPS in IDP (isodecylpelargonate)-1.6% wt. Cr content.

Formulation:		
AP 300 μ		39.5% wt.
AP 30 μ		39.5
Al 15 μ		5
ERLA 0510 ⎫		
DER 332 ⎬		14
HC 434 ⎭		
CrDIPS in IDP		2

The catalyst (including IDP plasticizer) level in the binder is, therefore, 12.5%. In our evaluation, we used a 10% level of CrDIPS/IDP in Telagen CT-ERLA 0510 binder mix. The active metal content is 0.16%; our 1% CrOct catalyzed systems contain 0.108% Cr.

Table XXVIII shows the results for a binder cure study using CrDIPS. It is effective at both ambient and 50°C, at least as effective as a similar loading of CrOct.

Figure 24 is a comparison of the effectiveness of a 5% loading of CrDIPS in the epoxide and aziridine cure of Telagen CT. In general, this catalyst appears more effective for the epoxide system than for the imine in that a higher extent of conversion is achieved. The chart below summarizes the catalytic behavior of CrDIPS in the Telagen system and compares it with CrOct.

Catalyst Loading (Wt. % in binder)	Wt. % Cr Metal In Binder	Time to 50% Conversion
CrDIPS (10)a/	0.16	20 hr.
CrDIPS (5)	0.08	2.5 days
CrOct (1)	0.11	1.5 days

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a/ CrDIPS in IDP - 1.6% wt. Cr content.

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* Chromium 2,6-diisopropyl salicylate.

TABLE XXVIII

CATALYSIS BY CrDIPS IN IDP[a]

Catalyst Level (Wt. %)	Temperature (°C)	Time (hr.)	% Rxn
10	R.T.	2.5	13.8
		4.5	24.6
		22.0	58.0
		27.0	64.0
		2 days	Cured (67)
10	50	2.5	60.5
		4.5	Cured (66)
5	R.T.	3.5	16.7
		27.0	55.1
		48.0	63.0
		7 days	Cured (67.6)
5	50	3.5	59.2
		6.5	66.5
		22.0	Cured (67)

[a]/ Cr content of catalyst mixture is 1.6%. Binder system: Telagen CT/ERLA 0510.
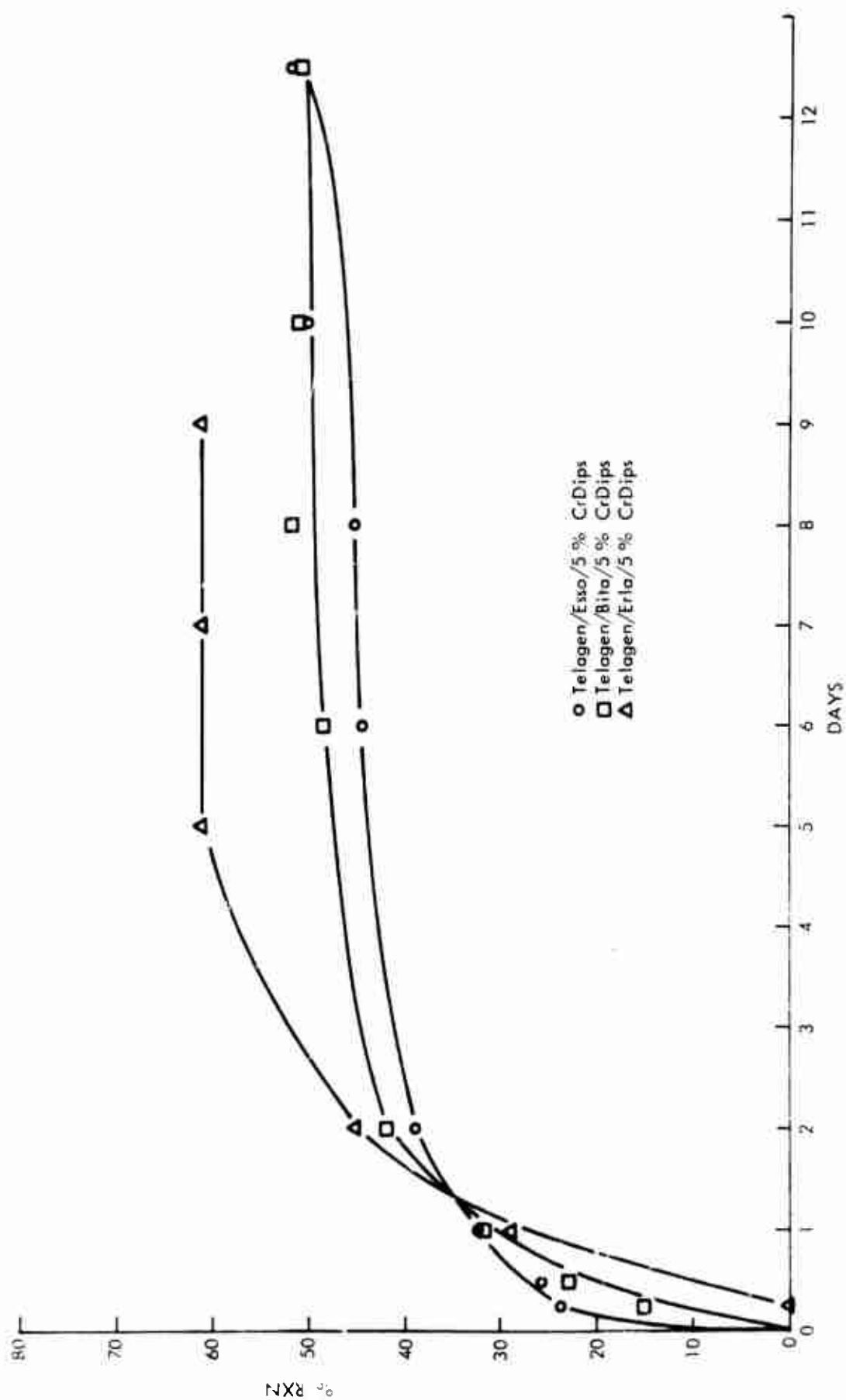
Figure 24 - The Catalysis of Telagen CT Cure by CrDIPS at 25°C

o Telogen/Esso/5 % CrDips
□ Telogen/Bito/5 % CrDips
△ Telogen/Erla/5 % CrDips

Figure 25 shows the effect of AP and Ammonyx T on CrDIPS catalyzed cure to Telagen CT and ERLA C510. The cure reaction pattern is unaffected by the presence of these ingredients.

As a result of these cure reaction rate observations, CrDIPS was selected for further screening at ABL of its performance in gumstocks and propellants.

D. PBAN Cure Studies and the Ammonyx T Question

ABL reported cure difficulties with PBAN polymer. The latter contains 4% by weight Ammonyx emulsifier. Two types of experiments were run to determine the nature of the interaction of the additive with the cure process: (1) GC model studies, and (2) binder cure studies with and without solids. Table XXIX summarizes the results of the model studies.

1. **Ammonyx effect in model systems**: The presence of Ammonyx at 1 and 4% levels in the model system has a slight acceleratory effect on the CrOct catalyzed reaction of AGE and EHA. The uncatalyzed controls (no CrOct) show a low level of reaction catalysis, especially at 50°C (93.6% conversion in 28 days at 4% Ammonyx T level). Hence, Ammonyx T displays the usual amine co-catalysis effect.

2. **Ammonyx effect in Telagen CT epoxide system:** Polymer cure studies were run in the Telagen CT/ERLA 0510 system in the presence of Ammonyx T and AP. These data are shown in Table XXX. The results are somewhat surprising; in the presence of 4% Ammonyx T, cure occurs at the same rate for both 1 and 0.5% catalyst loading. The presence of 5% AP in the sample leads to a 10% suppression of the rate of ester formation. These reactions were rerun to determine reproducibility.

Figure 26 shows the effect of AP and emulsifier level on cure behavior at 1 and 0.5% CrOct loadings. In this series, the presence of the Ammonyx T accelerated cure at both catalyst levels. For example, the time to 50% conversion for 1 and 0.5% CrOct loadings are 1.5 and 6.5 days, respectively. With the emulsifier these values become 0.5 day at 1% CrOct and 0.75 day at 0.5% catalyst level. One reaction containing 0.5% CrOct, 1% AP and 4% Ammonyx T behaved in an unexplainable fashion, that is, cure followed the pattern displayed by the other reactions until 40% conversion and then slowed considerably. Ultimate extent of reaction achieved was only 58% as compared to 70-73% for the others.

The presence of the emulsifier does accelerate and in some cases, alter, catalyzed reaction possibly by increasing the dispersion of the CrOct throughout the system and by solubilizing other potential trace reactants which may be present as contaminants in the other propellant components.
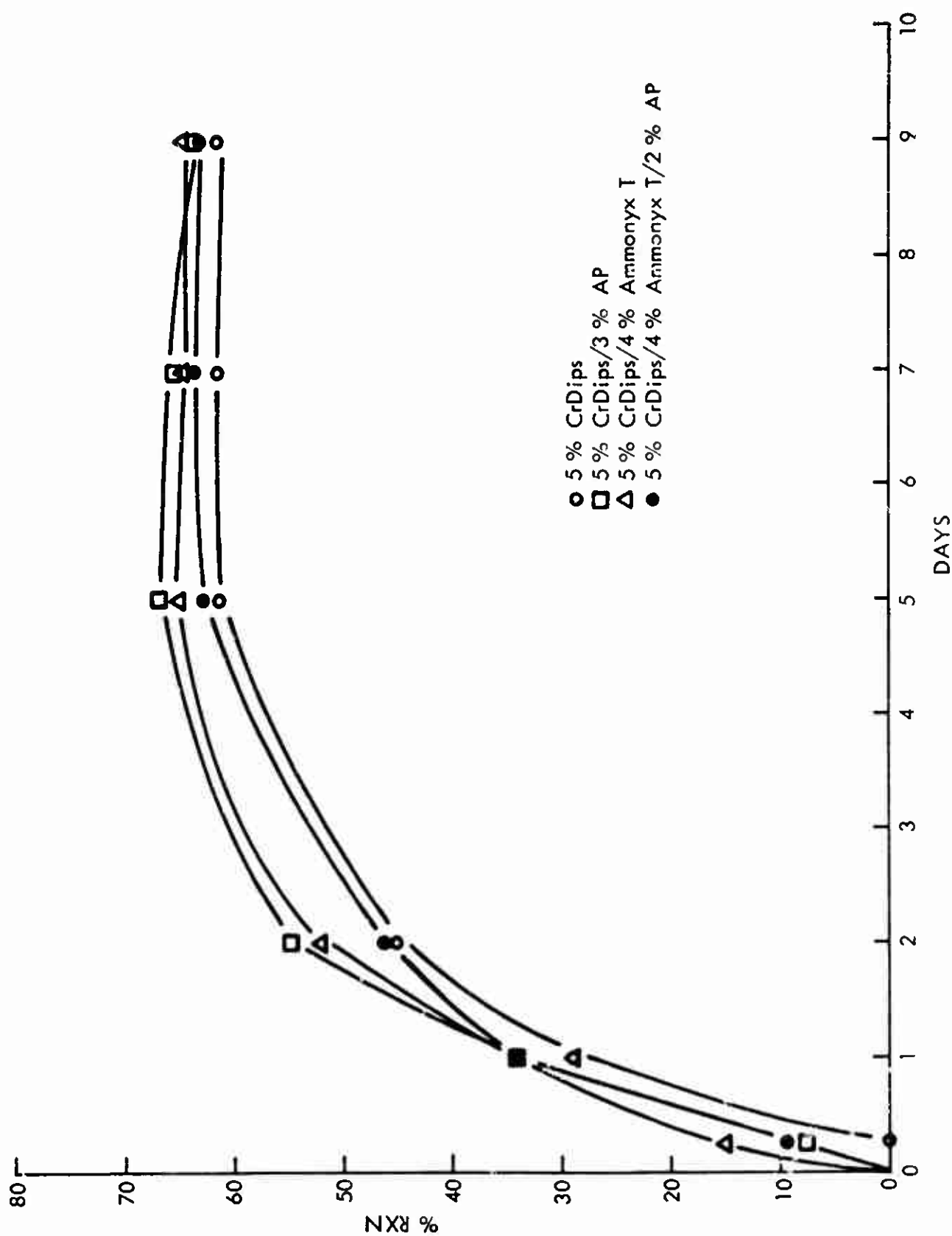
Figure 25 - The Effect of Ammonyx T and AP on the CrDIPS Catalyzed Cure of Telagen CT with ERLA510 at 25°C

o 5 % CrDips
□ 5 % CrDips/3 % AP
△ 5 % CrDips/4 % Ammonyx T
● 5 % CrDips/4 % Ammonyx T/2 % AP

DAYS

% RXN

TABLE XXIX

EFFECT OF AMMONYX T[a] ON REACTION OF EHA AND AGE

Weight % Ammonyx T	Catalyst Level[a]	Temperature (°C)	Time (hr.)	% Rxn	Stoichiometry
1	1	R.T.	5	23.5	1
			23	64.7	1
			48	82.4	1
			5 days	100.0	1
1	1	50	3	55.9	1
			23	97.9	1
4	1	R.T.	5	26.5	1
			23	67.6	1
			49	99.1	1
4	1	50	3.5	55.8	1
			24	95.0	1
1	0	R.T.	28 days	8.8	1
1	0	50	51	26.5	1
			13 days	35.4	1
			28 days	55.9	1
4	0	R.T.	5 days	11.6	1
			13 days	17.6	1
			28 days	23.5	1
4	0	50	1 day	8.8	1
			2 days	20.6	1
			5 days	44.1	1
			13 days	76.8	1
			28 days	93.6	

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a/ Cetyl-dimethylbenzylammonium chloride.

TABLE XXX

THE EFFECT OF AMMONYX T ON CURE OF TELAGEN CT WITH ERLA 0510

Catalyst Level	AP Level	Ammonyx Level	Temperature (°C)	Time (hr.)	% Rxn
1	0	4	R.T.	17.5	59.8
				23.0	61.4
				42.0	61.8
				6 days	Cured (65)
0.5	0	4	R.T.	17.5	58.5
				23.0	63.0
				42.0	64.6
0.5	5	4	R.T.	4.0	22.7
				17.0	43.0
				23.0	51.1
				42.0	51.5
				6 days	52.5
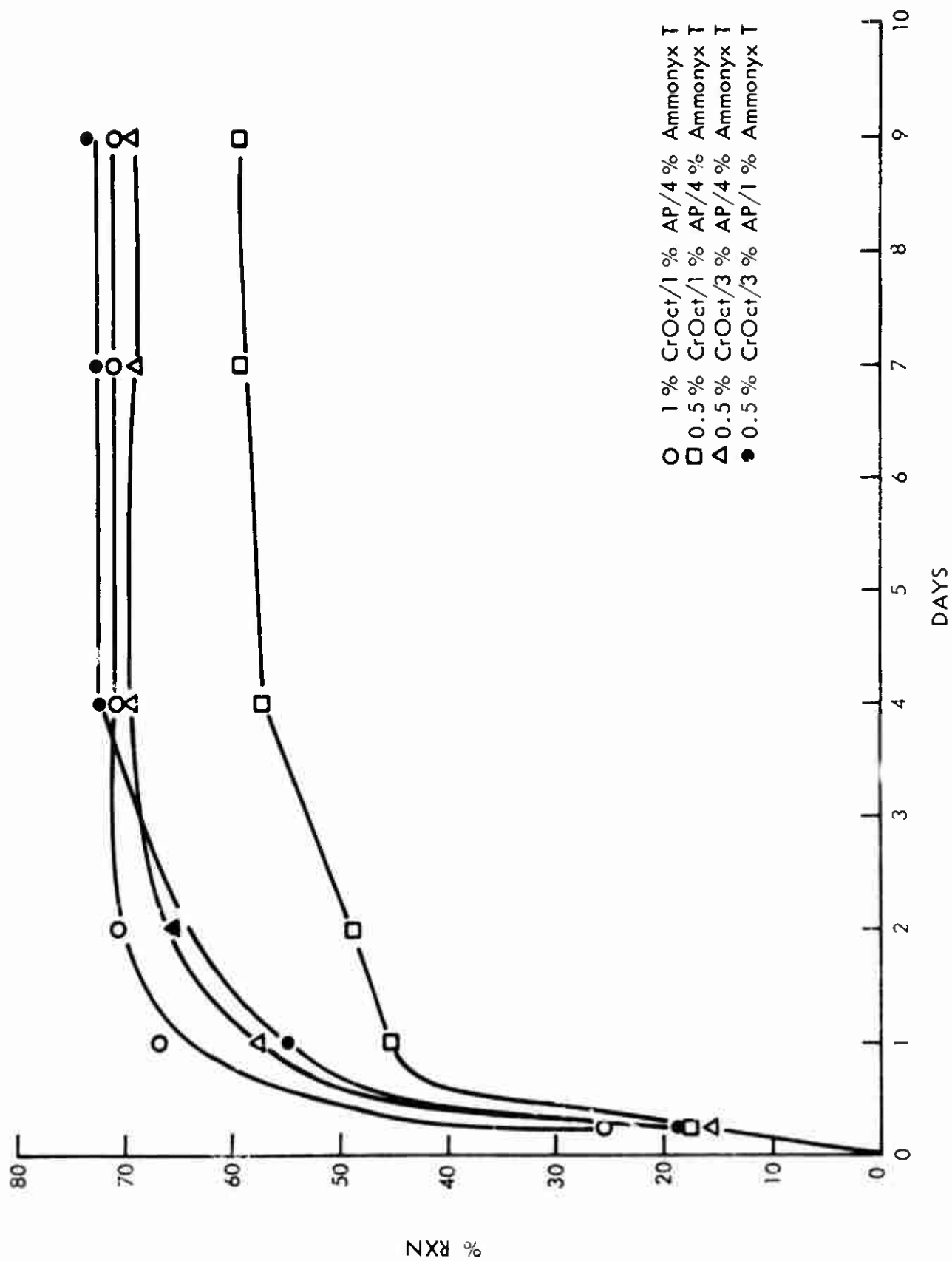
Figure 26 - The Effect of Ammonyx T and AP on the Cure of Telagen CT with ERLA510 at 25°C

○ 1 % CrOct/1 % AP/4 % Ammonyx T
□ 0.5 % CrOct/1 % AP/4 % Ammonyx T
△ 0.5 % CrOct/3 % AP/4 % Ammonyx T
● 0.5 % CrOct/3 % AP/1 % Ammonyx T

DAYS

% RXN

3. <u>PBAN cure studies</u>: An infrared calibration curve was prepared for
monitoring the change in ester and acid functionalities with time for the
CrOct catalyzed cure of PBAN and epoxide. These data are summarized in
Table XXXI. In general, the acid-ester conversion reaction proceeds as
expected as a function of catalyst quantity and temperature. A 3% loading
of AP tends to slow the 1% CrOct catalyzed reaction, as does Fe_2O_3.

The IR spectra for the PBAN cure systems show evidence of a side re-
action which occurs during later stages of cure. An absorbance at 6.3 -
6.4 μ appears after approximately 60% acid conversion and has continued to
grow. Functional groups of interest absorbing in this region include: CO_2^-,
NH_3^+ (deformation), NH_2^+ (deformation). This phenomena did not occur in the
Telagen-epoxide-Ammonyx T* mixes; hence, we attribute it to a PBAN inter-
action. The interaction could involve the nitrile of PBAN, the quarternary
ammonium salt (Ammonyx T), and the cure catalyst. The decreased availability
of carboxylic acid (with which CrOct will preferably coordinate) at this
stage of cure (> 60%) would then allow the side reaction to become increas-
ingly important. The net effect would be to prolong the time for cure to a
state giving desired mechanical properties.

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* Cetyl-dimethylbenzylammonium chloride.

TABLE XXXI

PBAN/ERLA 0510 CURE STUDY

Catalyst Level (% CrOct)	Temp. (°C)	Time (Days)	Extra Ingredient (%)	% Reaction Acid Consumed	Comment
1	25	(5 hr.)	--	27.3	No side rxn
		1	--	78.4	Side rxn beginning
		2	--	79.6	Side rxn continuing
		5	--	79.6	Side rxn continuing
1	50	(5 hr.)	--	76.2	Side rxn
		1	--	76.2	Side rxn
		2	--	76.2	Side rxn
		5	--	77.0	Side rxn
0.5	25	(6 hr.)	--	14.6	
		1	--	49.1	Side rxn beginning
		2	--	62.3	Side rxn continuing
		5	--	78.9	Side rxn continuing
0.5	50	(6 hr.)	--	49.6	Side rxn
		1	--	60.8	Side rxn continuing
		2	--	70.5	Side rxn continuing
		5	--	76.8	Side rxn continuing
1	25	(5 hr.)	3% AP	26.2	
		1		63.1	Side rxn apparent
		2		78.6	Side rxn continuing
		5		79.0	Side rxn continuing
1	50	(5 hr.)	3% AP	51.2	
		1		78.2	Side rxn apparent
		2		78.2	Side rxn continuing
		5		78.2	Side rxn continuing
1	25	(6 hr.)	1% Fe_2O_3	21.7	
		1		78.8	Side rxn apparent
		2		81.4	Side rxn continues
		5		83.7	Side rxn continues
1	50	(6 hr.)	1% Fe_2O_3	78.7	Side rxn apparent
		1		79.8	Side rxn continues
		2		79.8	Side rxn continues
		5		79.8	Side rxn continues

VI.

AZIRIDINE – ACID CATALYSIS STUDIES

A. Introduction

Like the epoxide, the aziridine group is also a strained, polar three-membered ring which undergoes reactions of the type similar to the epoxides, i.e., nucleophilic addition. Unlike the epoxide, however, aziridine reactivity is much more affected by substituents on and adjacent to the ring. Aziridines show a greater tendency than the epoxide to undergo rearrangement and homopolymerization reactions. Aziridines containing the P-N bond, while displaying acceptable cure reaction chemistry, tend to undergo bond cleavage at elevated temperatures. Acyl aziridines ($-\overset{\overset{O}{\|}}{C}-N\overline{\triangleleft}$) are prone to rearrange to oxazolines which, in turn, will also react with carboxylic acid but at a slower rate than the parent aziridine. The development and evaluation of aziridine curatives have been the subjects of an Air Force sponsored program (Ref. 8); based on results of that program and recommendation from the Air Force, two curatives were selected for primary use in our catalyst demonstration studies: HX-868 (1,3,5-Benzene-tris-carbonyl-2-ethylaziridine), and a new curative supplied by ESSO, 1,3,5-Benzene-tris-carbonyl-2,3-dimethyl-aziridine (AcAz).

In addition, MAPO and MAPS were used in certain experiments to provide a baseline for rate behavior since they are well-known and well characterized curatives.

B. Catalyst Selection Studies

A major contention of the mechanistic scheme proposed above for the catalysis of the acid-epoxide cure involves activation of the acid so as to make it more nucleophilic. Such a step facilitates attack on the ring of the curative (epoxide or aziridine) by the carboxylic acid and gives rise to the resulting ester. It is reasonable to assume that the mechanisms for epoxide and aziridine cures are similar in this respect. Thus, the information gathered from the epoxide studies was used as a starting point for catalyst selection for the aziridine system.

With this possible similarity of curing mechanisms in mind, several binder mixes were made using CrOct as catalyst and one of several aziridines as curatives (MAPO, MAPS, AcAz). In all cases, at a 1% CrOct loading, cure to a tough, nontacky binder was achieved at 25°C in less than 9 days. Figure 27 displays these results comparatively. The reaction behavior resembles that of the epoxide system, with several marked differences. First,
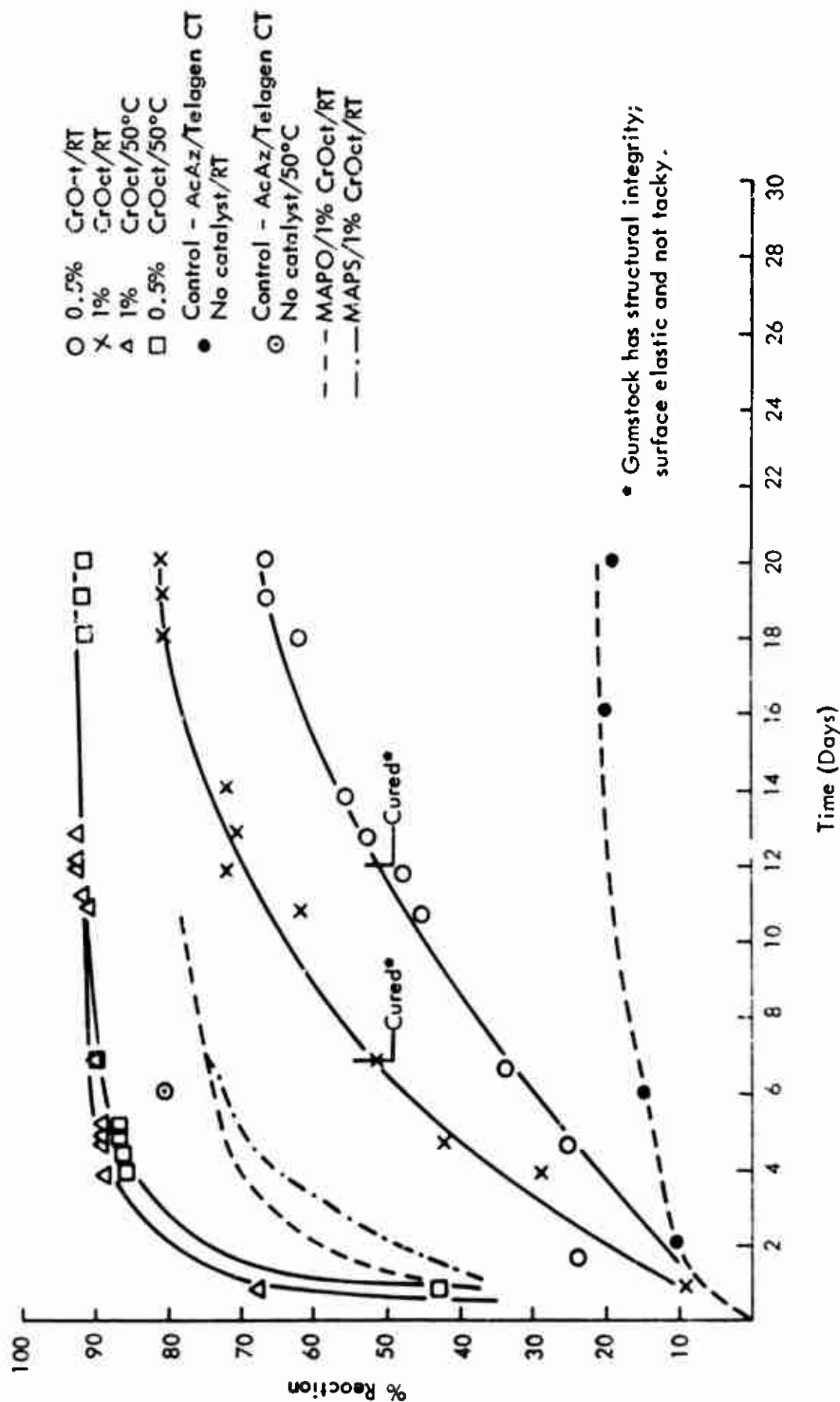
Figure 27 - Cure Rate Behavior of Telagen CT and Selected Aziridines Catalyzed by CrOct

thermal catalysis is an important parameter; at 50°C, there are no signifi-
cant differences in cure rate of the AcAz sample attributable to the different
catalyst concentrations (0.5 and 1% CrOct). In fact, an uncatalyzed control
(AcAz) at 50°C had reached 80% completion in 6 days while the analogous
catalyzed reactions were only at the 90% level. At 25°C, the difference in
conversion rates between 0.5 and 1.0% catalyst level is not as dramatic as
in a similar epoxide Telagen CT system. IR spectra show evidence of minor
side reactions during cure, probably oxazoline formation; this question is
discussed in detail below. Another unusual result is the high extent of
reaction noted for AcAz/Telagen CT, i.e., 90%. As previously noted in both
our studies and in the literature, 65 to 80% (depending on the individual
ingredients) is usually the conversion achieved in three-dimensional matrix
forming reactions.

Several organometallics of different structural characteristics were
evaluated for catalytic activity in the Telagen CT-acylaziridine (ESSO) system.
Only those mixtures containing CrOct or FeOct cured at ambient temperature;
as in the epoxide system all other additives failed to catalyze the reaction
in the desired time length. These results are summarized in Table XXXII.

TABLE XXXII

THE EFFECT OF SELECTED ORGANOMETALLICS ON THE
AMBIENT CURE OF TELAGEN CT WITH ACYL AZIRIDINE[b]

Catalyst[a]	Observation
Ferric Octoate	50% reaction in less than 7 days; cure in 10 days
Ferric Acetylacetonate	No cure
Ferrous Acetylacetonate	No cure
Chromium Acetylacetonate	Insoluble, no reaction
Stannous Octoate	No cure
Nickel Octoate	No cure

a/ All catalysts at the 1.0% by weight of binder level.
b/ ESSO product.

In summary, chromium octoate and to a lesser extent ferric octoate do
accelerate the reaction of aziridine curatives and Telagen CT at ambient
temperature. Visual cure is noted (i.e., sample is elastic and nontacky)
at 7 and 12 days (∿ 50% conversion) at 1.0 and 0.5% CrOct levels, respectively.

ABL reports CrOct to be less effective as a catalyst in the HX-868/ Telagen CT system than in the analogous epoxide system. We agree with ABL's evaluation based on the results of our studies with AcAz, which is reported to be a better curative in terms of stability, reactivity and stoichiometry than HX-868. The problem is rooted in the differences between the two classes of curatives. Epoxides are more stable instrinsically than aziridines and give more controllable and stoichiometric reactions with carboxylic acids.

Two conclusions are possible: (1) the catalytic trends are similar in both epoxide and aziridine systems. Aspects of the mechanism postulated for the cure of acid-epoxide systems are apparently applicable to the aziridine-acid reaction also (i.e., the same materials are effective as catalysts suggesting activation of the acid through coordination with the catalyst and attack by this intermediate on the curative); (2) differences in reactivity due to aziridine structure still exist in the catalyzed reaction, supporting further the acid activation mechanism in the organometallic reaction (i.e., if the aziridine were involved in the catalytic activation step a leveling effect on the rate might be expected throughout a series of aziridines of different structures since catalysis of the aziridine ring opening involves interaction at the nitrogen and not at the substituted carbons).

At this point chromium and iron salts (especially the octoates) were recommended for further evaluation in Phases III and IV (ABL) as ambient cure promoters in the aziridine cure system.

C. Side Reaction Problem

Figure 28 shows a comparison of the initial infrared spectrum for a mixture of Telagen CT, AcAz and chromium octoate with that for the same mixture after 13 days of reaction at room temperature. As expected, the carbonyl absorption due to carboxylic acid at 5.9 μ (2) decreases as ester carbonyl at 5.8 μ grows (1). Based on the disappearance of acid, reaction is approximately 70% complete after 13 days. The carbonyl absorption due to the acyl aziridine curative (3) also decreases with time as the 6.4 μ amide peak grows (4). The peak at 6.1 μ (5) due to unsaturation in the polymer (which should be an invariant in the spectrum) also shows an increase as reaction proceeds. In addition, several other absorbances grow, especially at 8.5 (7) and 8.9 μ (8). Considering the 6.1 μ peak growth first, two possibilities come to mind: (1) olefin formation through opening of the aziridine ring during cure or through elimination of acid from the product amide; (2) -C=N- absorption in oxazoline which could be formed under reaction conditions. Figure 29 displays the various reaction paths which can occur in the aziridine-carboxylic acid system.

93

Spectrum ot 0 hours

Spectrum of 13 days reaction (70% consumption of carboxylic acid)

Wavelength (microns)

1 – Ester carbonyl
2 – Acid carbonyl
3 – Carbonyl in ocyl aziridine
4 – Amide carbonyl

5 – Side product (olefin or C≡N from oxazoline)
6 – Side product
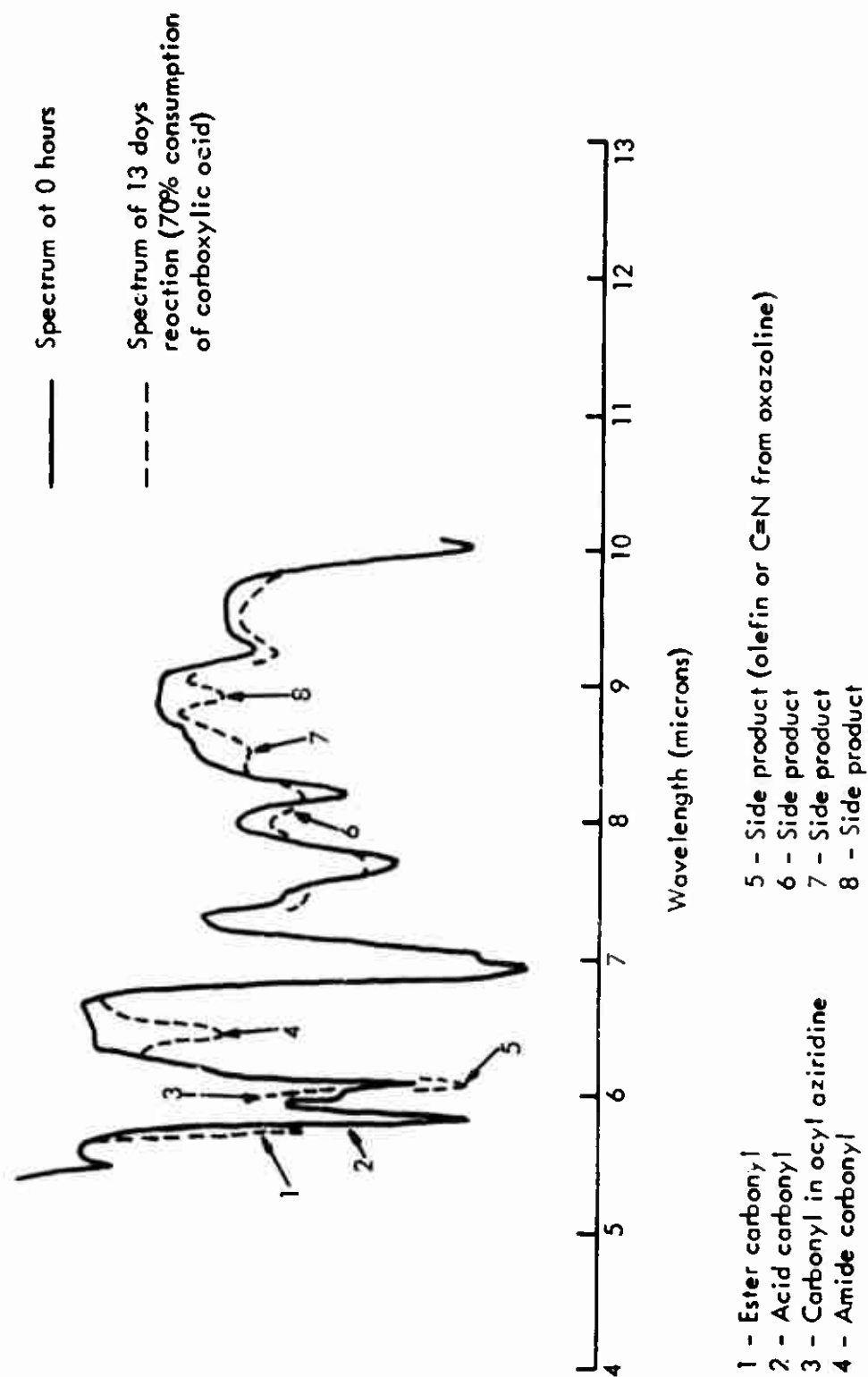7 – Side product
8 – Side product

Figure 28 – Infrared Spectrum of Telagen CT – AcAz Reaction

Workers at ESSO report (Ref. 8) acid elimination in the sulfonyl aziridine system to the extent of 40% of the product. However, they also claim excellent stoichiometry for the 2,3-dimethylaziridine-acid reaction. There are three major differences between these studies: temperature (ESSO—150°F, this study—25°C), the presence of the chromium catalyst, and the nature of the reaction system (ESSO—model, this study—gumstock).

Returning to the IR study, the increase in intensity at 6.1 μ can be due to either olefin formation or the -C=N- linkage in oxazoline. The absorptions at 8.5 and 8.9 are more clearly assignable to the -C-O- stretching vibration as found in the oxazoline. Hence the latter structure tends to explain major changes in the spectrum, which the olefin alone does not. One further point—if olefin formation is indeed occurring, it is unlikely that it would be formed through cure reversal (Figure 29, rxn 1) since acid is consistently consumed; no evidence has been found (in the IR) for carboxylic acid reformation. Rearrangement of the aziridine under the influence of the cure environment (rxn 2) would be a more logical explanation for olefin formation. The fact that these peaks do not appear in the IR spectrum of the Telagen CT-MAPO or MAPS reactions also suggests that the presence of these absorptions in acyl aziridine reactions is due to oxazoline formation, since neither the phosphine oxide nor the sulfide aziridine can rearrange to an oxazoline structure.

The control (uncatalyzed) AcAz-Telagen CT reaction run at 50°C also shows the same extra peak growth as catalyzed runs, indicating that the transformation in question is characteristic of acyl aziridine-carboxylic acid reaction. (The 8.8 to 8.9 μ peak is conspicuously absent from the spectra of the MAPO and MAPS cured polymers indicating the absorption in the AcAz system to be due to some group other than -C-O- in the ester formed from carboxylic acid attack on the imine ring.)

In summary, oxazoline formation may be occurring during the CrOct catalyzed cure of AcAz and Telagen CT, though olefin formation is also remotely possible.

Figure 29 - Possible Reaction Paths in the Telagen CT-AcAz Cure System

(1)

(2)

(desired product)

$\xrightarrow{\text{elimination}}$ R-C-N-CH-CH + HO-C-R''' , R'' = CH₃

[cat]?
olefin formation
via ring opening

oxazoline
formation

homopolymerization

etc.

D.   Aziridine Catalysis Studies

The effectiveness of CrOct and FeOct as catalysts for the aziridine cure system was explored further using Telagen CT and the curatives AcAz* and BITA.**   In addition, the effect of AP, Fe_2O_3, and water on imine cure was examined. Table XXXIIa lists the reaction rate data from these experiments.

In general, both organometallics are effective as cure catalysts, in that they promote the conversion of acid and imine to ester at ambient temperature in acceptable time periods.   The reaction appears stoichiometric in a practical sense, that is, acid consumption proceeds to a level expected in a cure reaction (60-80%) and absorbances noted in the IR spectra do not indicate significant or appreciable side reaction of curative (oxazoline formation).

Figure 30 displays the cure conversion behavior of the Telagen CT-BITA system.   As previously reported, the reaction rate is quite temperature-dependent.   In fact, rates are identical for the catalyzed 25°C mix and the uncatalyzed 50°C run.   A 1.0% loading of CrOct will promote the reaction to the 60% level in approximately 30 hr. while 8 days are required for the uncatalyzed gumstock cure.   Hence, CrOct is an effective catalyst for the BITA curative system.

Figure 31 is a similar display for the results from the study of Telagen CT-BITA cure promoted by 1% FeOct.   Conversion rates and thermal effects are identical to the CrOct system.   A plausible interpretation follows.   In the epoxide system, the reaction may be truly nucleophilic.   That is, the ring opens only (or predominantly) through attack by the activated acid.   Activation of the carboxylate (concentrating electronic charge by proton removal and coordination) is of critical importance in epoxide catalysis.   In contrast, the aziridine ring opens readily and the carboxyl group is acidic enough by itself to undergo condensation with the imine.   The organometallic thus merely facilitates a reaction which does not require the extensive activation needed in epoxide-carboxyl cure.

97
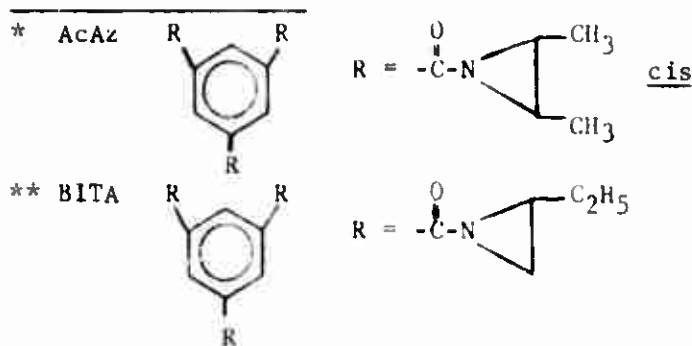
TABLE XXXIIa

CURE OF TELAGEN CT
WITH SELECTED AZIRIDINES

Curative	Catalyst (wt. %)	Extra Component (wt. %)	Temperature	Time	Meq. CO_2H Present	% Rxn
BITA	1% CrOct	-	R.T.	Initial	0.306	0.0
				24 hr.	0.128	58.2
				3	0.112	63.4
				4	0.113	63.1
				7	0.101	66.9
				10	0.10	67.3
BITA	1% CrOct	-	50	Initial	0.306	0.0
				2	0.190	37.9
				6	0.130	57.5
				19	0.110	64.1
				26	0.100	67.3
				43	0.099	67.6
				3 days	0.090	70.5
				4	0.100	67.3
				7	0.089	70.9
				10	0.86	71.8
BITA	0	-	R.T.	Initial	0.308	0.0
				1 day	0.206	33.1
				3	0.168	45.4
				4	0.143	53.6
				7	0.128	58.4
				9	0.109	64.6
				10	0.108	64.9
BITA	0	-	50	Initial	0.308	0.0
				3 hr.	0.264	14.2
				7	0.205	33.4
				20	0.150	51.3
				27	0.128	58.4
				43	0.124	59.7
				3 days	0.113	63.3
				4	0.109	64.6
				7	0.108	64.9
				8	0.106	65.5
				10	0.105	65.9

98

TABLE XXXII (Continued)

Curative	Catalyst (wt. %)	Extra Component (wt. %)	Temperature	Time	Meq. CO_2H Present	% Rxn
AcAz	1% CrOct	-	R.T.	Initial	0.314	0.0
				5.5 hr.	0.308	1.9
				2.5	0.250	20.4
				3 days	0.234	25.4
				6	0.204	35.0
				8	0.184	41.4
				9	0.180	42.6
AcAz	1% CrOct	-	50	Initial	0.314	0.0
				2 hr.	0.282	10.2
				7	0.249	20.7
				1 day	0.172	45.2
				2.5	0.111	64.6
				3	0.084	73.2
				6	0.056	82.2
				9	0.047	85.0
AcAz	1% FeOct	-	R.T.	Initial	0.330	0.0
				4 hr.	0.316	4.2
				2.5 days	0.178	46.1
				3	0.188	43.0
				6	0.177	46.4
				8	0.172	47.9
				9	0.173	47.6
AcAz	1% FeOct	-	50	Initial	0.330	0.0
				4 hr.	0.285	13.6
				7	0.257	22.1
				1 day	0.253	23.3
				2.5	0.210	36.4
				3	0.167	49.4
				6	0.135	59.1
				9	0.118	64.2
BITA	1% FeOct	-	R.T.	Initial	0.334	0.0
				1 day	0.132	60.4
				3	0.116	65.3
				4	0.120	64.1
				7	0.113	66.2
				9	0.125	62.5
				10	0.116	65.3

TABLE XXXII (Continued)

Curative	Catalyst (wt. %)	Extra Component (wt. %)	Temperature	Time	Meq. CO_2H Present	% Rxn
BITA	1% FeOct	-	50	Initial	0.334	0.0
				2 hr.	0.174	47.9
				4	0.120	64.1
				7	0.132	60.4
				24	0.114	65.8
				28	0.110	67.1
				2 days	0.110	67.1
				3	0.104	68.8
				4	0.100	70.1
				7	0.102	69.5
				8	0.074	77.8
				10	0.098	70.7
AcAz	0	5% AP	R.T.	Initial	0.382	0.0
				1 day	0.309	19.1
				3	0.328	14.1
				4	0.300	21.4
				7	0.300	21.4
				9	0.280	26.7
				10	0.282	26.2
AcAz	0	1% Fe_2O_3	R.T.	Initial	0.340	0.0
				1 day	0.311	8.5
				3	0.312	8.2
				4	0.300	11.7
				7	0.296	12.9
				9	0.289	15.0
				10	0.286	15.8
AcAz	1% CrOct	2 µl H_2O	R.T.	Initial	0.327	0.0
				4 hr.	0.298	8.8
				2 day	0.268	18.0
				3	0.236	27.8
				6	0.210	35.7
				8	0.197	39.7
				9	0.197	39.7

TABLE XXXII (Concluded)

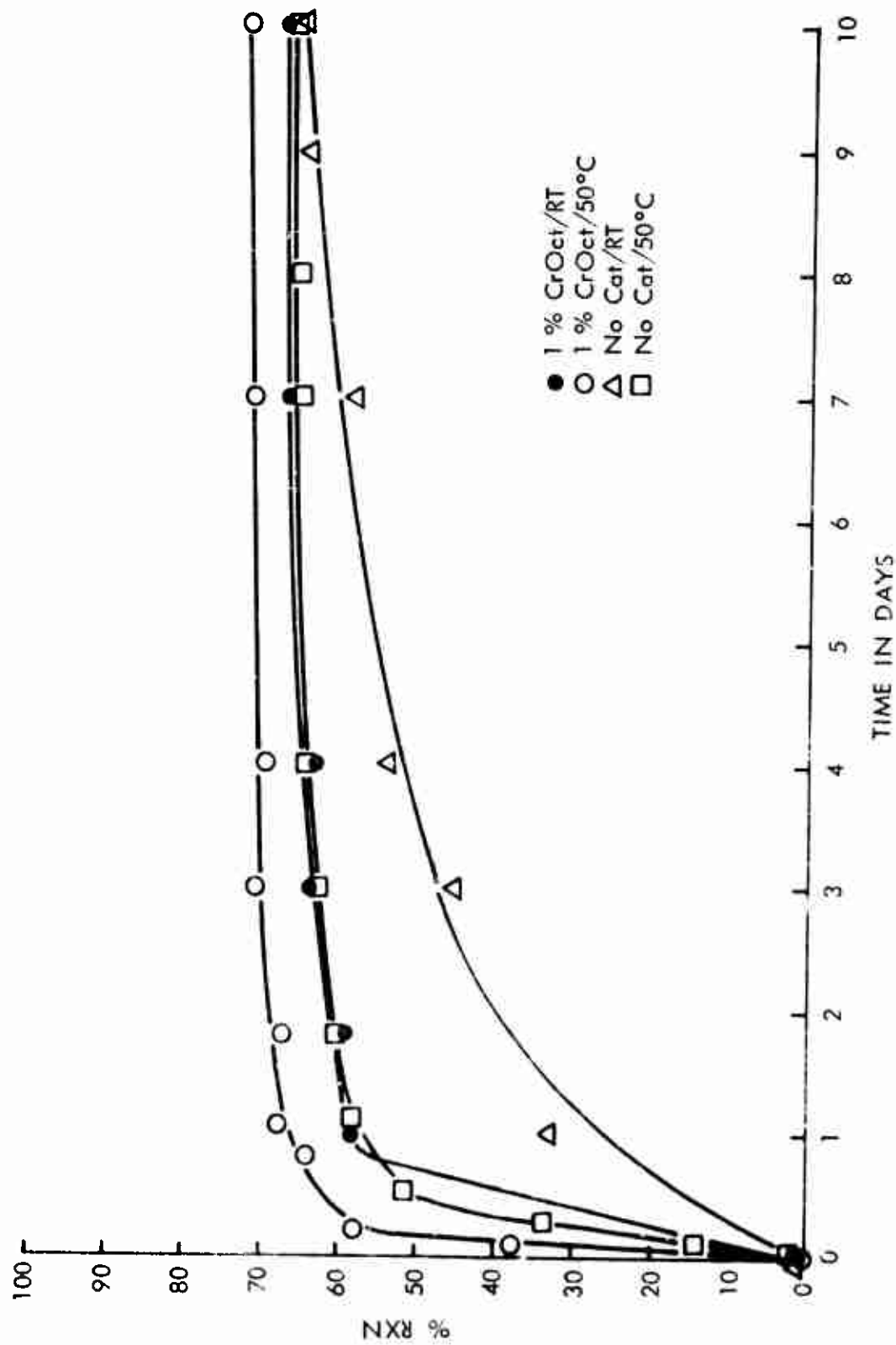| Curative	Catalyst (wt. %)	Extra Component (wt. %)	Temperature	Time	Meq. CO_2H Present	% Rxn
AcAz	1% CrOct	5% AP	R.T.	Initial	0.319	0.0
				5 hr.	0.298	6.5
				2 days	0.262	17.8
				3	0.231	27.6
				6	0.210	34.2
				8	0.198	37.9
				9	0.166	47.9
AcAz	1% CrOct	5% AP	50	Initial	0.319	0.0
				5 hr.	0.256	19.7
				1 day	0.179	43.9
				2	0.115	63.9
				3	0.090	71.7
				6	0.060	81.2
				7	0.053	83.4
				9	0.044	86.2
AcAz	1% CrOct	1% Fe_2O_3	R.T.	Initial	0.300	0.0
				2 days	0.270	10.0
				3	0.259	13.6
				6	0.231	23.0
				8	0.238	20.7
				9	0.210	30.0

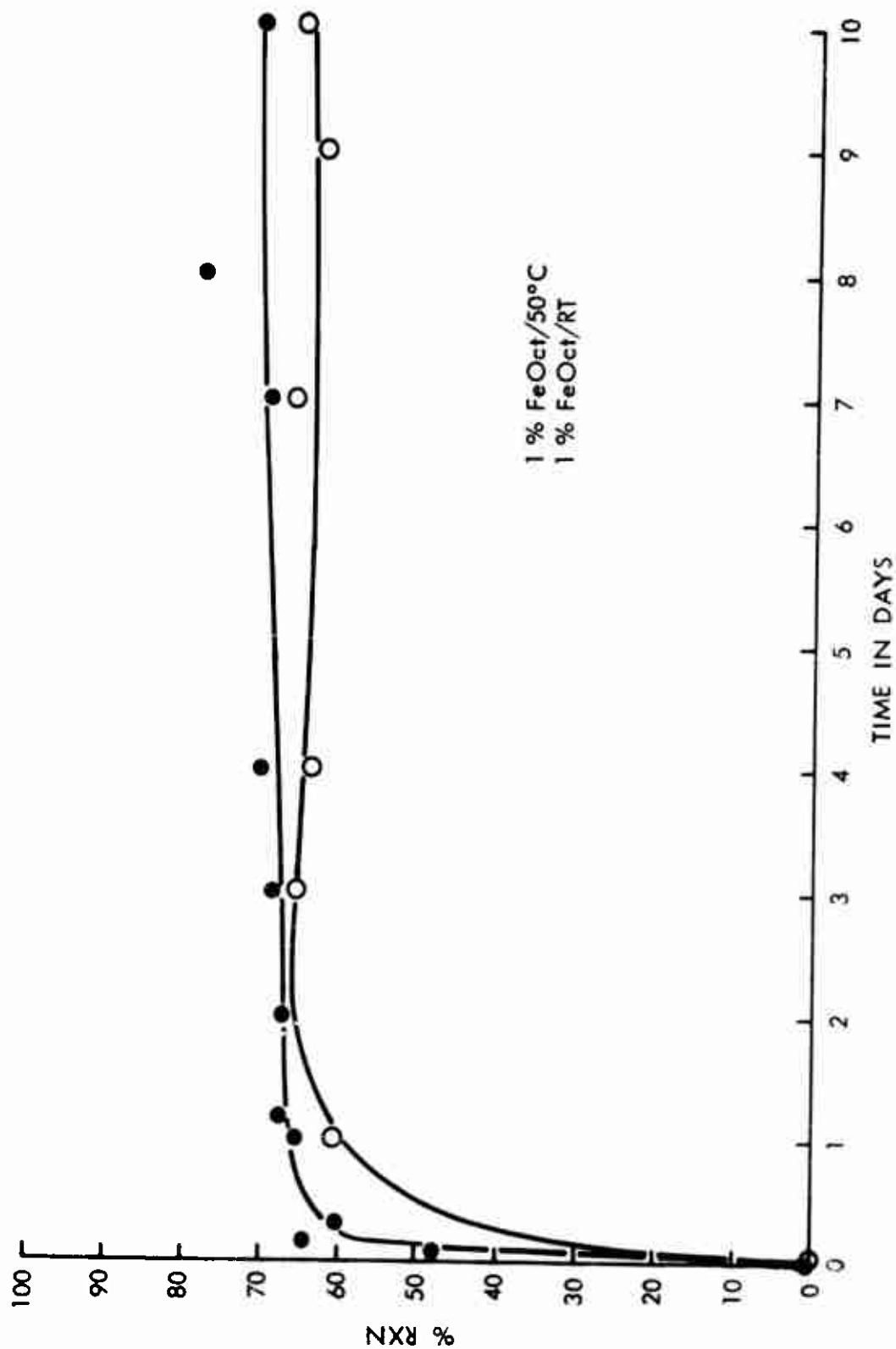Figure 30 - The Effect of CrOct Catalysis and Temperature on the Cure of Telagen CT with an Equivalent Amount of BITA

Figure 31 - Catalysis of the Cure of Collagen CT and BITA by FeOct

1 % FeOct/50°C
1 % FeOct/RT

TIME IN DAYS

% RXN

103

Figure 32 displays the rate patterns for the AcAz cure system catalyzed by the iron and chromium organometallics. At ambient temperatures, reaction is slower for both catalyst systems. Two factors may explain the difference between the two aziridine curatives: (1) AcAz is intrinsically more stable than BITA and should be less disposed to reaction; (2) possibly the most important difference is solubility--BITA is a liquid which readily dissolves in the polymer to give a transparent mixture. AcAz is a white powder which disperses in the Telagen CT to give an opaque gumstock. The fact that FeOct gives faster reaction rates, especially during initial stages of the conversion, can be attributed to the presence of diluent (mineral spirits) in the catalyst which would contribute to the solution and diffusion of reactants and catalyst. A recurring phenomenon is the high degree of conversion observed for the 50°C CrOct catalyzed system. It has been noted before and still remains the subject of speculation.

Study of the effect of propellant components and contaminants on the catalyzed cure of the aziridine binders began with an examination of the AcAz system. Figure 33 displays the effect of AP, Fe_2O_3, and H_2O on the CrOct promoted reaction. The presence of AP has shown no effect on rate and stoichiometry at either 25° or 50°C. The presence of Fe_2O_3 retards the the conversion at 25°C, possibly by aggravating the solubility situation.

Figure 34 shows the effect of AP and Fe_2O_3 on the cure system without CrOct. AcAz and Telagen CT at 25°C will react to approximately 15% conversion in the time period shown. Hence, the reactivity displayed in the Fe_2O_3 control would be due to the cure components themselves and not the extra ingredient. This suggests that Fe_2O_3 is interfering (rate retardation of $\sim$ 10%) with the catalytic process, perhaps by making it more difficult for CrOct to diffuse through the medium. A 5% loading of AP appears to catalyze the reaction slightly in the absence of CrOct (25% conversion in 10 days versus 15% for the cure functionalities alone).

In Figure 34, the effect of water in an amount equimolar to CrOct is shown; the rate pattern is identical within experimental error to that of the noncontaminated catalyzed system.

Hence, both FeOct and CrOct are effective cure catalysts for the acylaziridine-Telagen CT system. Rate differences between BITA and AcAz appear due to differences in solubility. AP and H_2O do not alter rate behavior in the AcAz cure reaction, though Fe_2O_3 does.

Supplemental aziridine evaluation data are reported in Table XXXIII.
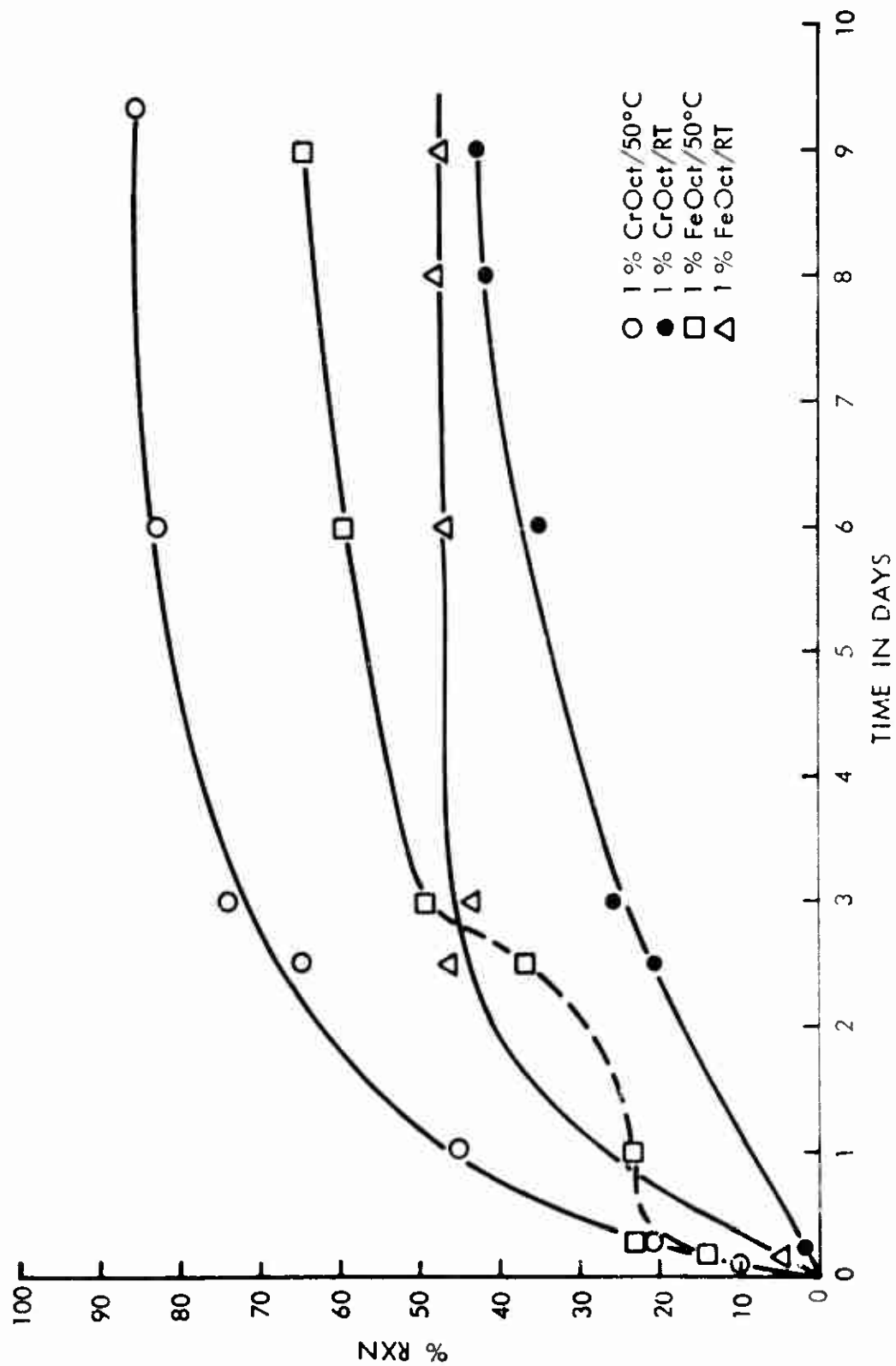
104

Figure 32 - The Effect of Catalysis and Temperature on the Cure of Telagen CT with AcAz, a Comparison of the Catalytic Effectiveness of CrOct and FeOct
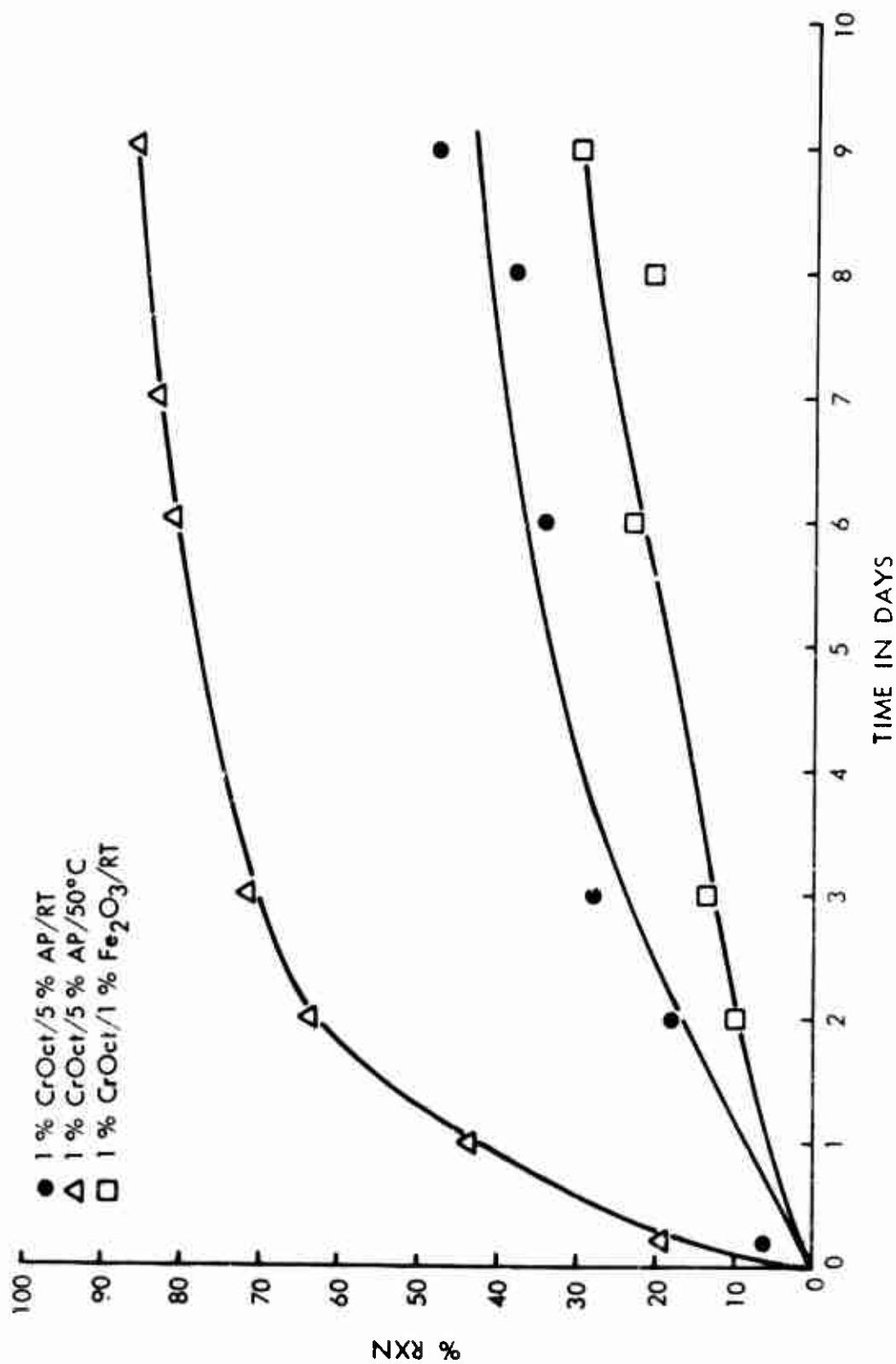
105

Figure 33 - The Effect of Extra-Ingredients on the CrOct Catalyzed Cure of Telagen CT and AcAz
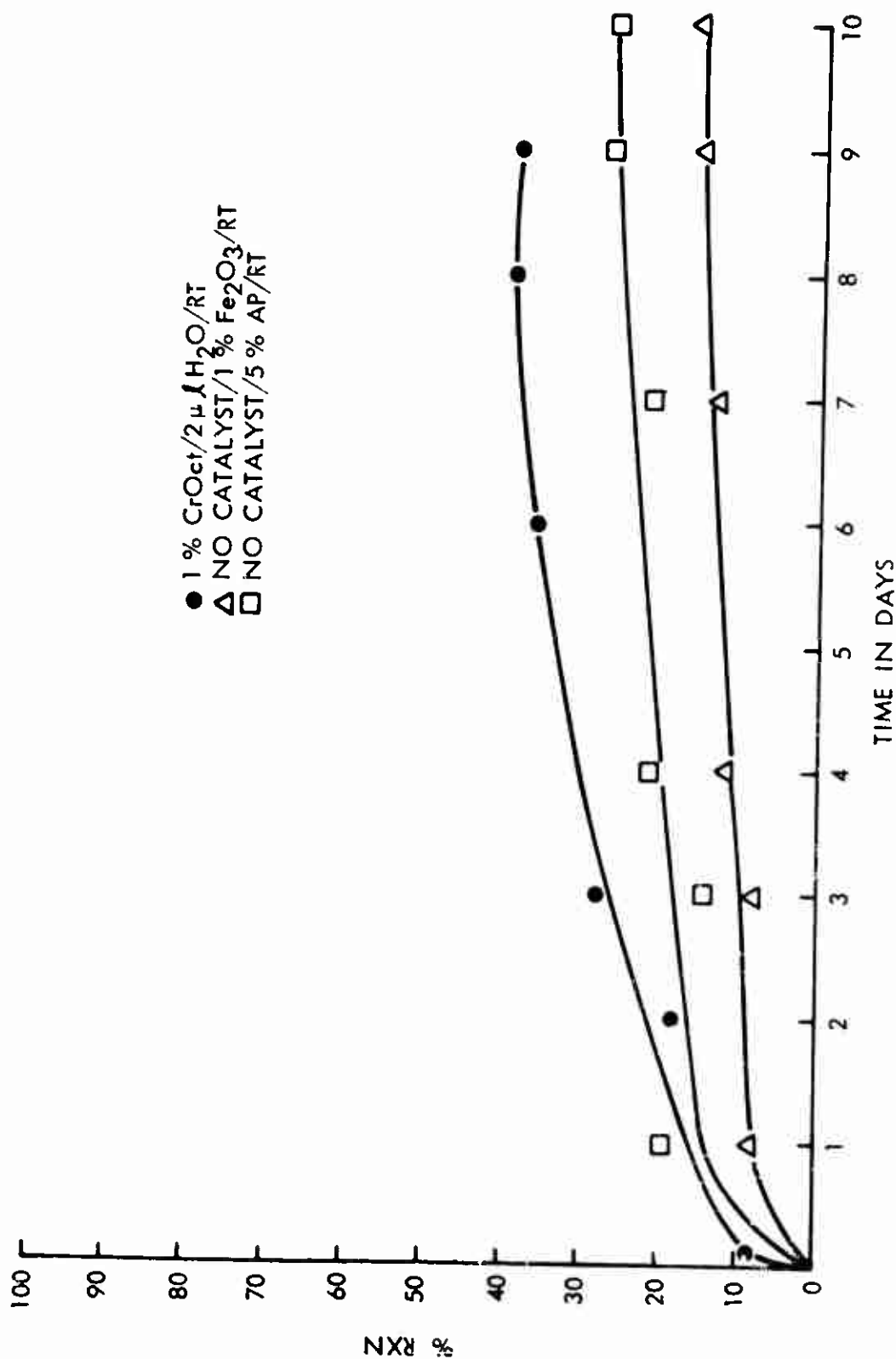
Figure 34 - The Effect of Extra-Ingredients (AP, Fe₂O₃, H₂O) on the Telagen CT-AcAz Cure System, Uncatalyzed Control

TABLE XXXIII

SUPPLEMENTAL AZIRIDINE CURE CATALYSIS DATA

System	Catalyst Level	Extra-Ingredient	Temperature	Time (hr.)	%Rxn
Telagen/BITA	0.5% CrOct	0	R.T.	2	9.7
				10	34.3
				23	42.2
				48	50.0
				3 days	53.4
				7 days	57.5
				10 days	58.5 Cured
Telagen/BITA	0.5% CrOct	5% AP	R.T.	10	28.8
				23	39.4
				48	47.7
				3 days	51.1
				7 days	55.7
				10 days	56.4 Cured
Telagen/AcAz	0.5% CrOct	5% AP		2	0
				10	1.0
				23	4.3
				48	10.4
				3 days	15.6
				7 days	22.6
				10 days	26.6
Telagen/BITA	1% CrOct	1% Fe_2O_3		5	23.2
				18.5	37.1
				48	44.3
				3 days	47.9
				7 days	45.4
				10 days	48.2
Telagen/BITA	1% FeOct	1% Fe_2O_3		5	23.7
				18.5	38.5
				48	47.0
				3 days	49.5
				7 days	54.1
				10 days	57.6
Telagen/AcAz	1% FeOct	1% Fe_2O_3		5	0.0
				18.5	10.0
				48	13.7
				3 days	18.4
				7 days	28.1
				10 days	28.4

As reported previously, AcAz reacts at a significantly slower rate than the other aziridine curatives (BITA, MAPO, MAPS). The 0.5% CrOct is too low a catalyst level to bring about the cure of Telagen with AcAz in a reasonable time period. The presence of AP slows the cure for both AcAz and BITA by 5-10%. Iron oxide slows the cure rate of the CrOct catalyzed system (Telagen/BITA). A similar retardation effect by Fe_2O_3 is noted in the FeOct catalyzed BITA/Telagen binder though it is not as pronounced as the chromium system.

E. Ammonyx T Effect in Aziridine System

Figures 35 and 36 show the effect of 4% by weight of Ammonyx T on the aziridine cure of Telagen CT. In the BITA system the presence of the Ammonyx alone promotes the reaction during early stages of cure but not as efficiently as CrOct. When AP and CrOct are present the emulsifier diminishes the efficiency of the Cr catalyst and the ultimate extent of reaction is 10% less than in the absence of Ammonyx T. In the AcAz system, the presence of the emulsifier has no significant effect on the cure rate.
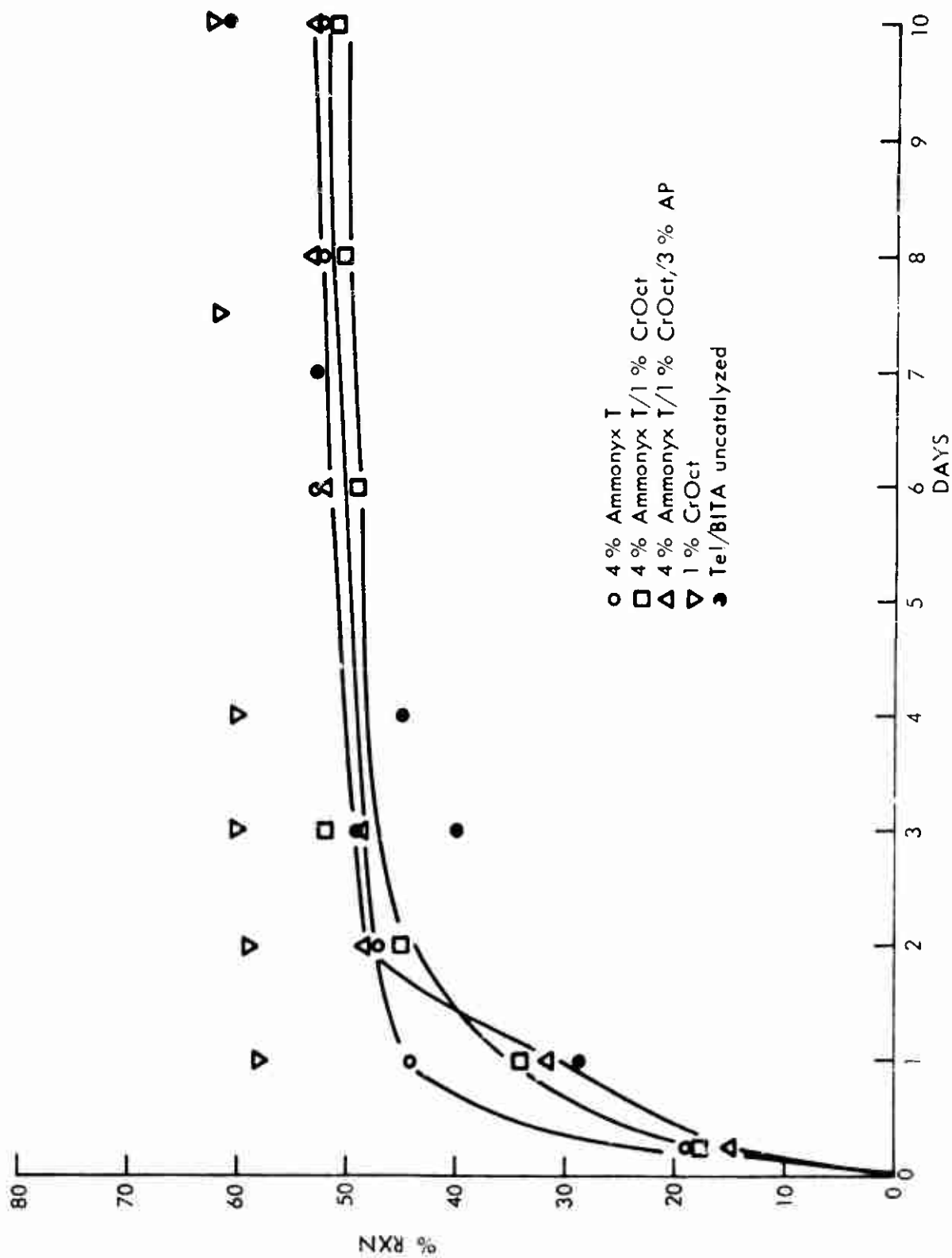
Figure 35 - The Effect of Ammonyx T on the Cure of Telagen CT with BITA at 25°C
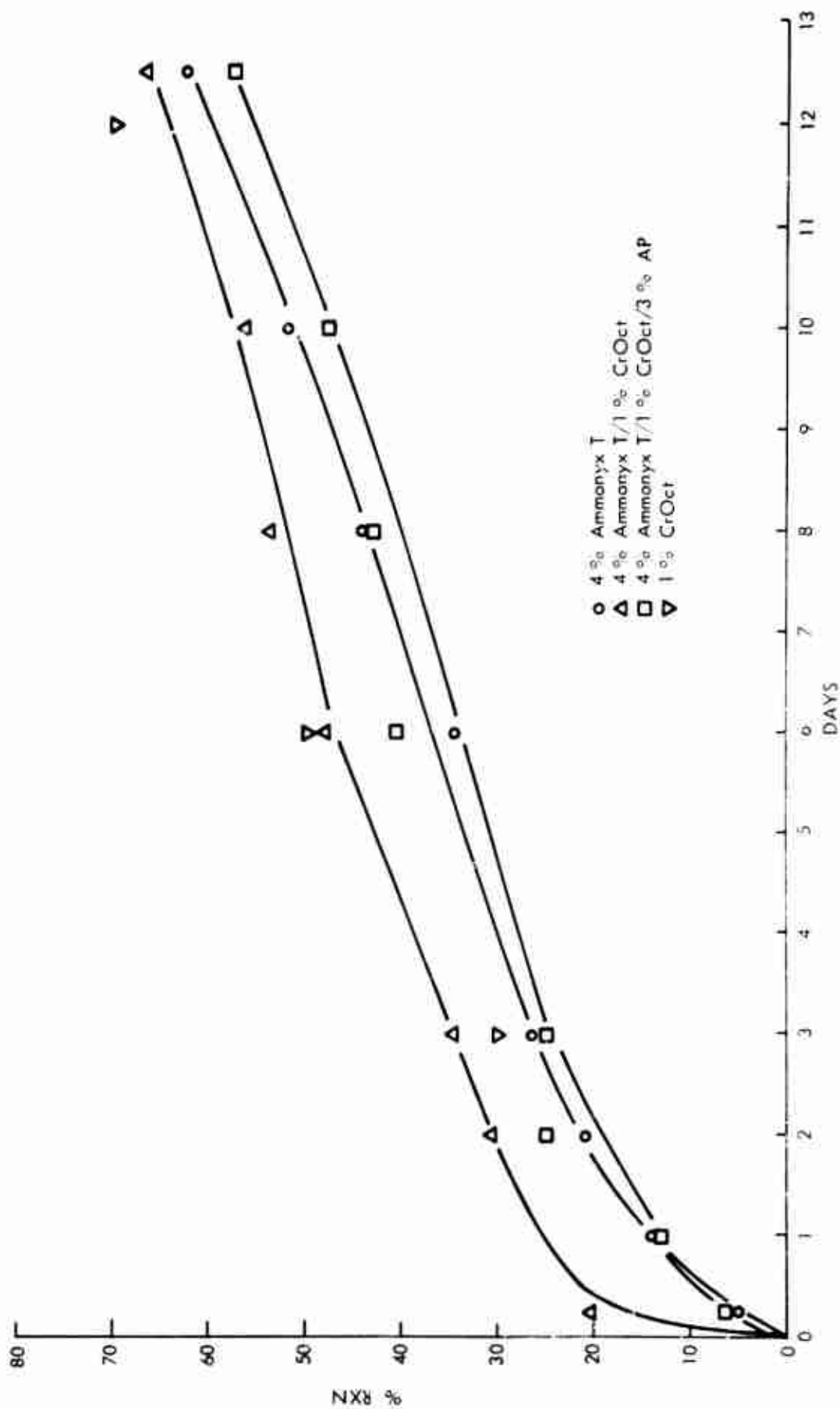
110

Figure 36 - The Effect of Ammonyx T on the Cure of Telagen CT with ESSO AcAz at 25°C
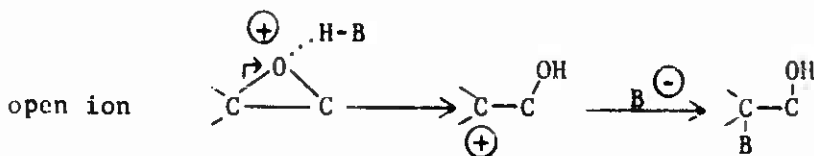
VII.

POSTCURE SURVEILLANCE

It has been demonstrated that chromium salts will catalyze the reaction of carboxylic acid and epoxide at room temperature rapidly and stoichiometrically. This catalyst is also effective in controlling the cure reaction of CT polymers with aziridines. The occurrence of postcure reactions will be a function of prevailing conditions in the propellant, that is, temperature, amount and relative proportions of unconverted cure functionality, etc.

A. Background - Epoxide Based Cure

The epoxide ring is a polar, strained structure susceptible to attack by nucleophilic species. The nature of the reaction is, of course, dependent on the type of attacking group, reaction conditions, and the type of catalysis, if any. Ring opening may proceed by way of acidic or basic mechanisms. In the basic system, attack occurs at the electron deficient carbon, leading to ring opening and the formation of an anionic product.
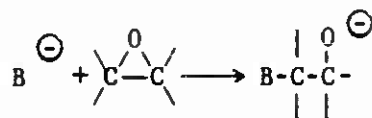
In the acidic situation, the epoxide oxygen is protonated and ring opening may occur in a number of ways, that is, in a concerted fashion, or an open ion two-step mechanism, or through a four-center associated intermediate.

112

four-center

$$\overset{\delta\ominus}{\underset{\delta\oplus\quad\delta\oplus}{\overset{O}{C \diagup\!\!\!\diagdown C}}} \longrightarrow \quad C - \overset{O}{\underset{}{C}} \cdots H\cdots B \longrightarrow \overset{OH\ B}{\underset{|}{C - C}}$$
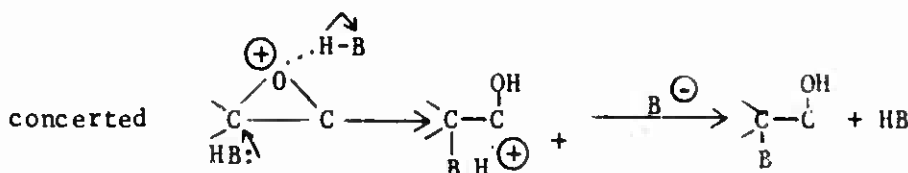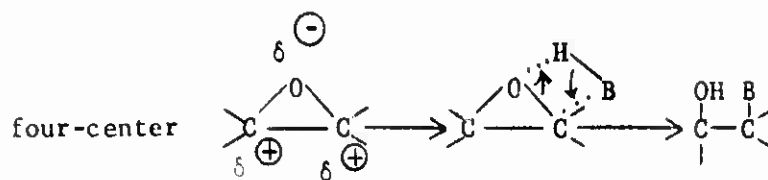
The reaction of specific interest here is the addition esterification of a carboxylic acid with an epoxide.

$$R-\overset{O}{\underset{}{C}}-OH \;+\; \overset{O}{C - C} \longrightarrow R-\overset{O}{\underset{}{C}}-O-\overset{|}{\underset{|}{C}}-\overset{OH}{C} \qquad (1)$$

Several competing reactions are possible depending on conditions and reactant concentrations.

condensation
esterification
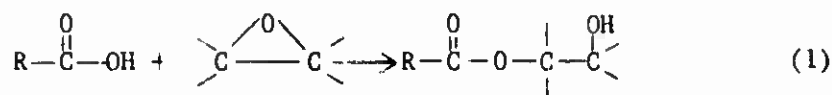$$R-\overset{O}{\underset{}{C}}-OH \;+\; ROH \rightleftharpoons R-\overset{O}{\underset{}{C}}-O-R \;+\; H_2O \qquad (2)$$
$$\text{(product)}$$

etherification
$$ROH \;+\; \overset{O}{C - C} \longrightarrow R'-O-C-\overset{OH}{\underset{|}{C}}- \qquad (3)$$

etc. $R'\!\!-\!\!\overset{}{(}C-C$

$$R' = R''-\overset{O}{\underset{}{C}}-O-CH_2-CH$$
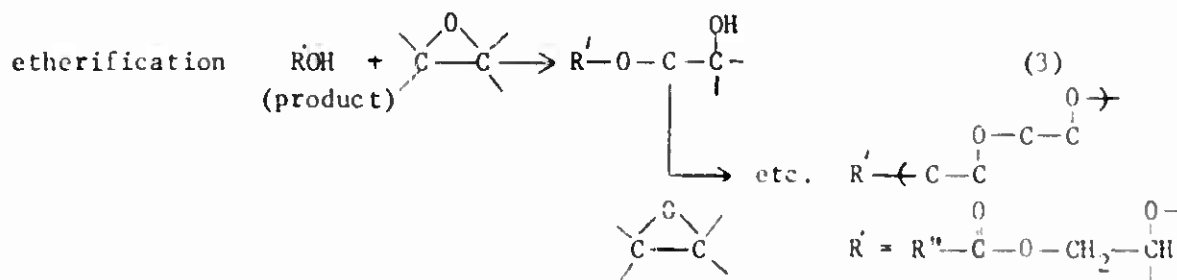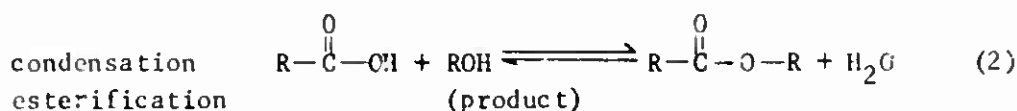
Reaction (2) is favored by high temperature (200°C), excess alcohol, and water removal. (Under actual polymerization or curing conditions, equilibrium conditions prevail and this reaction is essentially suppressed since the only route for water removal is evaporation and/or reaction with epoxide to form glycols.)

Etherification, reaction (3), is favored by low temperature (less than 200°C), excess epoxide, and acid catalysis. This route will lead to a polyether polymer of the following type $R-\overset{O}{\underset{}{C}}-O(\overset{}{\underset{|}{C}}-\overset{}{\underset{|}{C}}-O)_n H$.

113

In the presence of a basic catalyst the reaction is specific to addition esterification (No. 1); only after complete consumption of acid will excess epoxide react with the product alcohol via the etherification route.

Hence, mild temperature, base catalysis, and equivalent concentrations of reactant acid and epoxide are conditions specific to reaction 1. Acid catalysis and low temperature favor etherification; excess epoxide will optimize this route. In the absence of acid or base catalysis, temperature becomes the controlling reaction parameter, with etherification being increasingly suppressed at higher temperatures.

In addition, several other interactions are possible; oxidative cross-linking of olefin groups present in the binder promoted by the cure catalyst; degradation (e.g., dehydration, decarboxylation) of the ester product through the influence of the metal.

B. Surveillance Studies Undertaken

The intent of these studies was to determine the role which the cure catalyst may play in propellant aging. Specific interactions of interest (due to the presence of catalyst) include: reversal of the cure linkage, catalytic decomposition of the product ester, other reactions within the product (e.g., oxidative cross-linking of olefin groups), and promotion of reactions due to other propellant components. To separate the variables in the complex propellant, a series of surveillance studies is under way from simple model studies (to examine potential fundamental chemical interactions) to 40-lb. propellant blocks. The aging studies include the following:

1. Model reaction systems with and without additional propellant ingredients: These were intended to determine situations of cure reversal and/or reaction of the product with the added ingredient attributable to the presence of the catalyst.

2. Cured binders: The intent is the same as above.

3. Excess epoxide studies: Both, model and polymer, were examined to assess the importance of etherification reactions as described above.

4. Excess acid studies: Both model and polymer, to determine the importance of postcure esterification reactions.

5. Whole propellant surveillance: Mechanical property changes with time on large samples.

114

C. Binder Surveillance - Results

Cured binder systems under ambient storage for extended time periods were examined by infrared for evidence of postcure reactions. An IR spectrum was taken of each sample (cured and stored between salt plates); the ester content was measured and compared to the 30-day reading (a time at which cure has usually occurred) for the sample to determine whether cure continued (increase in ester) or whether cure degradation occurred (decrease in ester content). In addition, the spectrum was examined for the formation of or changes in other peaks, a situation which would indicate degradation of other groups within the polymer, or postcure reaction. The results from the stored samples are shown in Table XXXIV. Without exception, no significant infrared detectable chemical change has occurred in the epoxide cured systems after extended periods of ambient storage. This holds true for even those samples containing the various propellant solids. Only the aziridine curative AcAz shows evidence of a slow continuing ester formation reaction.

It can be safely concluded that the presence of the chromium salts (octoate, oleate) in a cured binder does not adversely affect the stability of the cure or the binder itself. In fact, the ambient cured and stored acid/epoxide based binders are chemically stable for periods of up to 22 months even in the presence of propellant solids.

The results for aziridine systems show a dependence upon the specific curative used, as expected. However, the only aging effect attributable to the presence of the Cr catalyst is continued ester formation with the slow reacting AcAz compound.

D. Model System Surveillance - Results

Products of model reactions run at 25°C were stored at ambient temperature and at 50°C. These were analyzed after extended storage and the results compared to data obtained within about 2 weeks after initiation of the reactions. The results of these analyses are shown in Tables XXXV and XXXVI. A note of explanation is needed concerning this table. The short lines represent the relative concentrations of the side products and their position in the gas chromatogram, relative to the height and major product (long line). In the figure, where the major product is shown off-scale, the total amounts of the minor components never exceed 1% of the total theoretical yield.

In general, no change has occurred in the product composition of most of the CrOct catalyzed reactions. It is difficult to determine whether the minor products noted in the samples containing extra ingredients are due to solution of that ingredient or actual postcure reactions. Regardless, the presence of the cure catalyst does not cause reversal nor does it promote postcure reactions to any appreciable degree.

115

TABLE XXXIV

CUREO BINOER SURVE1LLANCE

Cure System	Temperature[a]	Time (month)	New Peaks[b]	Cure Reversal[c]	Continued Cure (%)[d]	Other[e]
Tel/AcAz/0.5% CrOct	R.T.	11	No	No	54	No
Tel/AcAz/0.5% CrOct 5% AP	R.T.	11	No	No	55	No
Tel/BITA/1% CrOct 1% Fe$_2$O$_3$	R.T.	11	No	No	No	No
Tel/BITA/1% FeOct 1% Fe$_2$O$_3$	R.T.	11	No	No	8	No
Tel/AcAz/1% FeOct 1% Fe$_2$O$_3$	R.T.	11	No	No	50	No
Tel/AcAz/Control	R.T.	10	No	No	50	No
Tel/AcAz/5% AP	R.T.	10	No	No	35	No
Tel/BITA/1% Fe$_2$O$_3$	R.T.	10	No	No	No	No
Tel/BITA/1% CrOct 5% AP	R.T.	10	No	No	2	No
Tel/BITA/1% CrOct 2 µl. H$_2$O	R.T.	10	No	No	5	No
Tel/AcAz/4% Ammonyx T	R.T.	10	No	No	40	No
Tel/AcAz/1% CrOct 4% Ammonyx T	R.T.	10	No	No	40	No
Tel/AcAz/1% CrOct 4% Ammonyx T/3% AP	R.T.	10	No	No	35	No
Tel/BITA/4% Ammonyx T	R.T.	10	No	No	15	No
Tel/BITA/4% Ammonyx T 1% CrOct	R.T.	10	No	No	10	No
Tel/BITA/4% Ammonyx T 1% CrOct/4% AP	R.T.	10	No	No	No	No
Tel/AcAz/5% CrOIPS	R.T.	10	No	No	30	No
Tel/BITA/5% CrOIPS	R.T.	10	No	No	No	No
Tel/ERLA/5% CrOIPS	R.T.	10	No	No	No	No
Tel/ERLA/5% CrDIPS 3% AP	R.T.	10	No	No	No	No
Tel/ERLA/5% CrDIPS 4% Ammonyx T	R.T.	9	No	No	No	No
Tel/ERLA/5% CrD1PS 2% AP/4% Ammonyx T	R.T.	9	No	No	No	No
Tel/ERLA/1% CrOct 1% AP/4% Ammonyx T	R.T.	9	No	No	No	No
Tel/ERLA/0.5% CrOct 1% AP/4% Ammonyx T	R.T.	9	No	No	No	No
Tel/ERLA/0.5% CrOct 3% AP/4% Ammonyx T	R.T.	9	No	No	No	No
Tel/ERLA/0.5% CrOct 3% AP/1% Ammonyx T	R.T.	9	No	No	No	No
Tel/ERLA/1% CrOct	R.T.	24	No	No	No	No
Tel/ERLA/1% CrOleate	R.T.	24	No	No	No	No
Tel/ERLA/6% FeOct	R.T.	23	No	No	No	No
Tel/1% CrOct	R.T.	22	No	No	No	No
Tel/(23%) ERLA/1% CrOct[f]	R.T.	22	No	No	No	No
Tel/(~6%) ERLA/1% CrOct[f]	R.T.	22	No	No	No	No
Tel/(13%) ERLA/1% CrOct[f]	R.T.	22	No	No	No	No

TABLE XXXIV (Concluded)

Cure System	Temperature[e]	Time (month)	New Peaks[b]	Cure Reversal[c]	Continued Cure (%)[d]	Other[e]
Tel/(97%) ERLA/1% CrOct[f]	R.T.	22	No	No	No	No
Tel/(120%) ERLA/1% CrOct[f]	R.T.	22	No	No	No	No
Tel/(144%) ERLA/1% CrOct[f]	R.T.	22	No	No	No	No
Tel/(166%) ERLA/1% CrOct[f]	R.T.	22	No	No	No	No
Tel/ERLA/0.2% CrOct	R.T.	18	No	No	No	No
Tel/MAPS/1% FeOct	R.T.	18	No	No	No	No
Tel/AcAz/1% FeOct	R.T.	16	No	No	20	No
Tel/ERLA/1% TOPA 0.4% CrOct	R.T.	16	No	No	No	No
Tel/AcAz/0.5% CrOct	R.T.	15	No	No	5	No
Tel/AcAz/1% CrOct	R.T.	15	No	No	20	No
Tel/BITA/1% CrOct	R.T.	12	No	No	No	No
Tel/AcAz/1% CrOct	R.T.	12	No	Nc	5	No
Tel/AcAz/1% FeOct	R.T.	12	No	No	30	No
Tel/BITA/1% FeOct	R.T.	12	No	No	No	No
Tel/AcAz/1% CrOct 2 μl. H_2O	R.T.	12	No	No	10	No
Tel/AcAz/1% CrOct 5% AP	R.T.	12	No	No	10	No
Tel/AcAz/1% CrOct 1% Fe_2O_3	R.T.	12	No	No	15	No
Tel/ERLA/5% CrOIPS	R.T.	11	No	No	No	No
XS Tel/ERLA/1% CrOct	R.T.	11	No	No	No	N
Tel/ERLA/1% CrOct 4% Ammonyx T	R.T.	11	No	Yes	No	No
Tel/ERLA/0.5% CrOct 4% Ammonyx T	R.T.	11	40	No	No	No
Tel/ERLA/0.5% CrOct 5% AP/4% Ammonyx T	R.T.	11	No	No	No	No
XS Tel/ERLA/0.5% CrOct	R.T.	11	No	No	No	No
Tel/XS ERLA/0.5% CrOct	R.T.	11	No	No	No	No
Tel/BITA/0.5% CrOct	R.T.	11	No	No	No	No
Tel/BITA/0.5% CrOct 5% AP	R.T.	11	No	No	No	No

e/ Temperature of storage.

b/ The appearance of new peaks in the spectrum would indicate the formation of a new chemical entity during storage.

c/ Cure reversal would be indicated by loss of ester relative to previous reading.

d/ Continued cure would be indicated by an increase in ester absorbence accompanied by a decrease in the remaining acid content.

e/ This category would include observations not falling under the other three classifications.

f/ The numbers in parentheses indicate the percent of the stoichiometric amount of epoxide used in the experiment. These mixes were used for the establishment of a calibration curve.

TABLE XXXV

SURVEILLANCE OF MODEL REACTION SAMPLES

AGE	COMPOSITION	REACTION PRODUCTS
mo.	1% CrOct/5%AP/Age/Ena	
mo.	0.1% CrOct/5%AP/Age/Ena	
mo.	1% CrOct/PA/Age	
mo.	2% CrOct/PA/Age	
mo.	1% CrOct/OA/Age (shaken)	
mo.	2% CrOct/OA/Age	
mo.	1% CrOct/9µlH$_2$O/Age/Ena	
mo.	1% CrOct/18µlH$_2$O/Age/Ena	
mo.	1% CrOct/90µlH$_2$O/Age/Ena	
mo.	1% CrOct/0.5%Fe$_2$O$_3$/Age/Ena	
mo.	1% CrOct/1%Fe$_2$O$_3$/Age/Ena	
mo.	10% CrOct/Age (Homopolymerization)	
mo.	6% CrOct/Age/Ena	

118

TABLE XXXV (Continued)

REACTION PRODUCTS

AGE	COMPOSITION
R.O.	1% CrOct/1% Al/Age/Ena
R.O.	1% CrOct/0.5%Roccal Age/Ena
R.O.	1% CrOct/0.5% Phenol-B-N Age/Ena
R.O.	1% CrOct/1%Oxazolidine/Age/
R.O.	0.5%CrOct/0.5%FeOct/Age/Ena
R.O.	1% CrOct(ROC)/Age/Ena
R.O.	1% CrOct/PA/Age/Ena
R.O.	.4% CrOct/PA/Age/Ena
R.O.	1% CrOct/OA/Age/Ena
R.O.	0.4% CrOct/OA/Age/Ena
R.O.	1% CrOct/1% TDPA/Age/Ena
R.O.	1% CrOct/% TDPA/Age/Ena
R.O.	20% CrOct/Age/Ena
	0% CrOct/Age/En

119

TABLE XXXV (Concluded)

AGE	COMPOSITION	REACTION PRODUCTS
2 mo.	4% CrOct/Age/Enh	
2 mo.	1% CrOct/xs Age/OA	
14 mo.	1% CrOct/Ester Product/Age	
14 mo.	1% CrOct/HNO3/Age/Ena	
14 mo.	No CrOct/HNO3/Age/Ena	
14 mo.	1% CrOct/NH4OH/Age/Ena	
14 mo.	No CrOct/NH4OH/Age/Ena	
14 mo.	1% CrOct/RONO2/Age/Ena	
14 mo.	No CrOct/RONO2/Age/Ena	

RONO2 (ROC) = n-propylnitrate
= Research Organic Chemicals, Inc.
* = desired ester product
Phenyl-B-N = Phenyl-B-naphtylamine
TDPA = antioxidant triisopropenylamine
OA = octanoic acid
PA = propionic acid

120

TABLE XXXVI

SURVEILLANCE OF MODEL REACTION SAMPLES (50°C STORAGE)

Age	Composition	Reaction Products
3 mo.	2% Cr-neo/Age/Eha	*
23 mo.	1% CrOct/Age/Eha/5% AP	*
23 mo.	1% CrOct/Age/Eha/18 µl H2O	*
23 mo.	1% CrOct/Age/Eha/9 µl H2O	*
23 mo.	1% CrOct/Age/Eha/90 µl H2O	*
23 mo.	Product/Tol/9 µl H2O	*
23 mo.	1% Cr-neo/Age/Eha/90 µl H2O	*
23 mo.	1% CrOlea/Age/Eha/9 µl H2O	*
23 mo.	1% CrOlea/Age/Eha/90 µl H2O	*
23 mo.	0.5% Fe2O3/Age/Eha	*
23 mo.	1% CrOct/0.5% Fe2O3/Age/Eha	*
23 mo.	1% CrOct/1% Fe2O3/Age/Eha	
23 mo.	1% Fe2O3/Age/Eha	
23 mo.	1% HMB/Age/Eha	*

121

TABLE XXXVI (Continued)

Age	Composition	Reaction Products
mo.	2% Fe(Oct)₂/Age/Eha	
mo.	2% Fe(Oct)₂/18 μl H₂O/Age/Eha	
mo.	0.5% CrOct/0.5% Fe(Oct)₂/Age/Eha	
20 mo.	1% TFG/Age/Eha	
20 mo.	1% DPLC/Age/Eha	
20 mo.	1% TPL/Age/Eha	
20 mo.	1% TEL/Age/Eha	
20 mo.	1% CrOct(ROC)/Age/Eha	
20 mo.	1% FeOct(ROC)/Age/Eha	
20 mo.	1% PbOct(ROC)/Age/Eha	
20 mo.	1% CrFormate(ROC)/Age/Eha	
20 mo.	1% TPLC/Age/Eha	
19 mo.	1% CrOct/PA/Age/Eha	
19 mo.	C.4% CrOct/PA/Age/Eha	

TABLE XXXVI (Continued)

Age	Composition	Reaction Products
19 mo.	1% CrOct/OA/Age/Eha	*
19 mo.	0.4% CrOct/OA/Age/Eha	* *
19 mo.	1% CrHep/Age/Eha	*
19 mo.	1% CrHex/Age/Eha	*
19 mo.	0.5% TDPA/Age/Eha	*
19 mo.	1% TDPA/Age/Eha	*
19 mo.	2% TDPA/Age/Eha	*
19 mo.	1% CrOct/1% TDPA/Age/Eha	*
19 mo.	0.5% TDPA/0.5% Fe_2O_3/Age/Eha	*
19 mo.	9 μl $HClO_4$/Age/Eha	
19 mo.	0.5% TDPA/0.5% Fe_2O_3/0.5% CrOct/Age/Eha	*
19 mo.	1% CrOct/10 μl $HClO_4$/Age/Eha	*
19 mo.	1% CrOct/100 μl $HClO_4$/Age/Eha	
19 mo.	1% CrOct/5 μl $HClO_4$/Age/Eha	*

123

TABLE XXXVI (Continued)

Age	Composition	Reaction Products
17 mo.	1% CrOct/OA/Age	*
17 mo.	2% CrOct/OA/Age	*
17 mo.	0.5% CrHep/OA/Age	*
17 mo.	1% CrHep/OA/Age	*
16 mo.	1% CrOct/xs Age/Eha	*
16 mo.	2% CrOct/xs Age/OA	*
16 mo.	1% CrOct/xs Age/Product	*
16 mo.	1% Pyridine/Age/OA	*
16 mo.	1% TEA/Age/OA	*
15 mo.	1% CrOct/HNO$_3$/Age/Eha	*
15 mo.	No CrOct/HNO$_3$/Age/Eha	*
15 mo.	1% CrOct/NH$_4$OH/Age/Eha	*
15 mo.	No CrOct/NH$_4$OH/Age/Eha	*
15 mo.	1% CrOct/RONO$_2$/Age/Eha	*
15 mo.	No CrOct/RONO$_2$/Age/Eha	*

TABLE XXXVI (Concluded)

Age	Composition	Reaction Products
13 mo.	1$ CrOct/1$ AmyxT/Age/Eha	*
13 mo.	1$ CrOct/4$ AmyxT/Age/Eha	*
13 mo.	No CrOct/1$ AmyxT/Age/Eha	*
13 mo.	No CrOct/4$ AmyxT/Age/Eha	*
13 mo.	No CrOct/HF/Age/Eha	
13 mo.	1$ CrOct/HF/Age/Eha	*
13 mo.	1$ CrOct/N$_2$O/Age/Eha	*

RONO$_2$ = n-propynitrate
(ROC) = Research Chemicals, Inc.
* = desired ester product
Cr-neo = Chromium-neo-decanoate
CrOlea = Chromium Oleate
TCMB = B-trichloro-N-trimethylborazine
TPG = Triphenyl germanium
DPLDC = Diphenyllead dichloride
TPLC = Triphenyllead chloride
TPL = Tetraphenyllead
TEL = Tetraethyllead

CrHep = Chromium Heptanoate
CrHex = Chromium Hexanoate
TDPA = antioxidant thiodiphenylamine
Product = ester product from large batch of catalyzed Age and Eha
AmyxT = Ammonyx T

125

VIII.

PROPELLANT STUDIES

A. Objective of Propellant Studies

The overall objective of this portion of the program was the demonstration of the ambient-temperature-cure catalyst system which Midwest Research Institute (MRI) studies indicated was the best for CTPB propellants.

B. Approach

The following six carboxyl binder systems were examined: the carboxy-terminated prepolymers, Telagen and HC-434, and the terpolymer polybutadiene acrylic acid acryloritrile (PBAN) cured with either epoxides or aziridines. This portion of the program was divided into two phases. The first part, "Catalyst Behavior with Composite Propellant Ingredients" (Phase III of the overall program), consisted of basic studies of various catalysts which were suggested by the results obtained at MRI. The basic studies were performed on the six binder systems and involved: (1) determining relative effectiveness of various catalysts, (2) effects of normal propellant solid ingredients on catalyzed ambient cure, and (3) selection of catalyst concentrations to be tested in actual composite propellant formulations. The second part of the ABL program, "Scale-Up Demonstration of Cure Catalysis" (Phase IV of the overall program), consisted of: (1) selection of baseline propellant formulations which would have the optimum cure catalyst needed to yield good slurry pot life, reasonably short ambient cure time and good cured mechanical properties, (2) determination of the effect of various other propellant ingredients and likely contaminants on catalyzed ambient cure, and (3) evaluation of the aging characteristics of solid propellants formulated with these cure catalyst systems.

IX.

CATALYSIS BEHAVIOR WITH COMPOSITE PROPELLANT INGREDIENTS

A. Summary

The Telagen prepolymer was found, in gumstock studies, to cure at
ambient temperature with the triepoxide ERLA-0510 in 1 week with 0.40%,
and in 2 weeks with 0.37% chromium octoate (CrOct) cure catalyst.
Ordinary propellant solids such as ammonimum perchlorate (AP), aluminum,
and Fe_2O_3 do not affect the cure significantly. The HC-434 prepolymer
behaves in a similar fashion in gumstock studies. The potential cure
catalysts, chromium oleate and chromium 2,6-diisopropyl salicylate were
found to be less effective than CrOct at equal Cr concentrations.

Ambient cure of the two CTFB prepolymers with the aziridine HX-868
required about twice as much CrOct catalyst as did the expoxide-cured
systems.

Normal propellant solids interfered with the CrOct ambient cure of
binders based on the PBAN prepolymer. The PBAN-aziridine system was very
slow to cure, even with high CrOct concentrations.

In each of the six binder systems, catalyst levels were selected to
be used for the first 1-lb. propellant mixes to be made in Phase IV.

B. Discussion of Results

1. Procedure: Model compound studies performed at Midwest
Research Institute indicated that the chromium coordination compounds
were the most effective catalysts for carboxy binder systems. Therefore,
ABL examined three such compounds; chromium 2-ethyl hexanoate (generally
called chromium octoate or CrOct), chromium oleate and chromium 2,6-
diisopropyl salicylate (CrDIPS). Testing consisted entirely of gumstock
studies during this phase.

Binder studies were conducted to determine the concentration of
cure catalyst which would provide cure at ambient temperature ($25 \pm 1°C$)
in a reasonable time period (1 to 2 weeks). The binders consisted of the
prepolymer, curing agents, IDP or DOA plasticizer and cure catalyst. Some
also contained various solid fillers. The degree of cure was followed by
periodically measuring mechanical properties, gel content, and swelling.

127

Experimentally the cure study procedure was to prepare 30-g mixes of the binder consisting of 70% polymer, the specified quantity of cure catalyst and solids, and the remainder was plasticizer. The binder was evacuated and cast into four 8-in. long by 1/4-in. diameter Teflon tubes. After curing for the specified time period, the binder was removed from the Teflon tube and specimens were prepared. Duplicate mechanical property specimens (1/4-in. by 1-in. cyclinders) were prepared by epoxy bonding to wooden end tabs. The samples were pulled on an Instron tester at a strain rate of 1 in/in/min until 35% elongation. The secant modulus at 30% elongation was then calculated. Samples were not tested till break because, frequently, the binder was stronger than the bond to the wooden end tab which resulted in specimens breaking at the bond rather than within the binder phase. The bond was always strong enough to permit testing the specimen to 30% elongation.

Gel content was determined on a 1-g. binder sample by a 48-hr. methylene chloride extraction which was followed by a 4-day acetone extraction if AP was present. Gel samples had a 1/16-in. web thickness. Linear swelling was determined on duplicate 1-in. long specimens in contact with benzene for 3 days. The benzene was replaced with fresh solvent on each of the first 2 days.

2. Chromium Octoate:

a. Telagen gumstocks: It was determined that nearly complete cure of Telagen will take place within a week with 0.40% CrOct present and within 2 weeks at the 0.37% catalyst level. Mechanical property data which form part of the basis for this conclusion are shown in Figures 37 and 38. The presence of AP filler seems to accelerate the binder cure at the higher catalyst level, while aluminum and Fe_2O_3 (not shown) do not affect the cure. At the 0.2 or 0.3% CrOct levels, cure was not complete after 2 weeks. In both of these studies, and in others performed with the Telagen prepolymer, mechanical preperties gel content, or swell, all change slightly after 2 or 3 weeks, indicating that cure is still progressing slowly.

An experiment was performed to measure the viscosity of Telagen binder with 0.40% chromium octoate as a function of time, to determine if this system had a reasonable pot life at 26°C. The results, given in Figure 39, show that the viscosity of the binder triples in about 4 hr. This is an acceptable increase. To meet the goals of the program, the propellant must have at least a 4-hr. pot life (≤ 35 K_p) and a reasonable ambient temperature cure time of 2 weeks or less.

Binder gumstock studies were performed with Telagen and the aziridine HX-868 as a preliminary to propellant manufacturing. In the first study it was learned that the cure reaction was slower than the
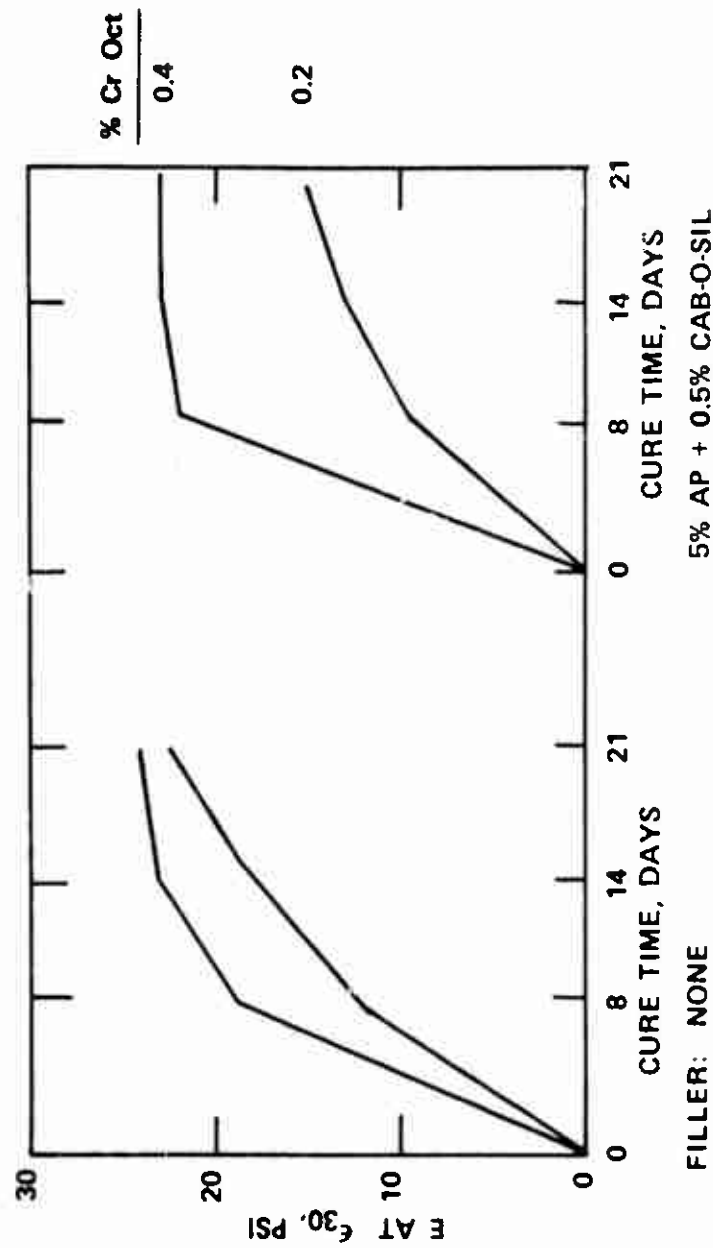
128

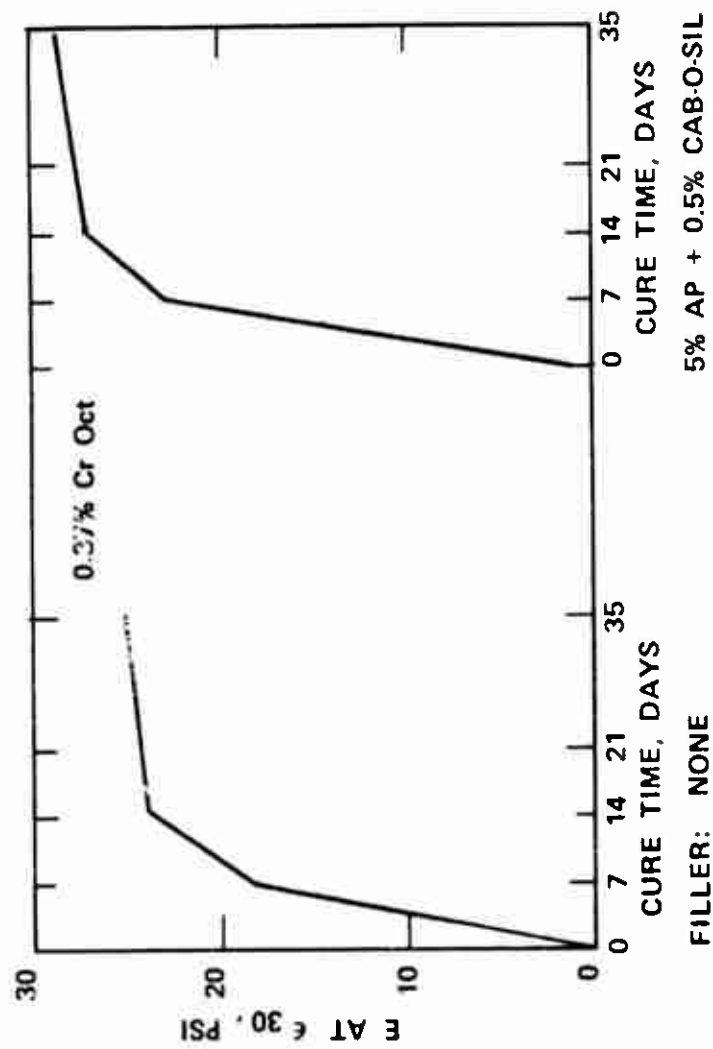Figure 37 - Secant Modulus at 30% Elongation vs. Cure Time for Telagen Binders X196-16

129

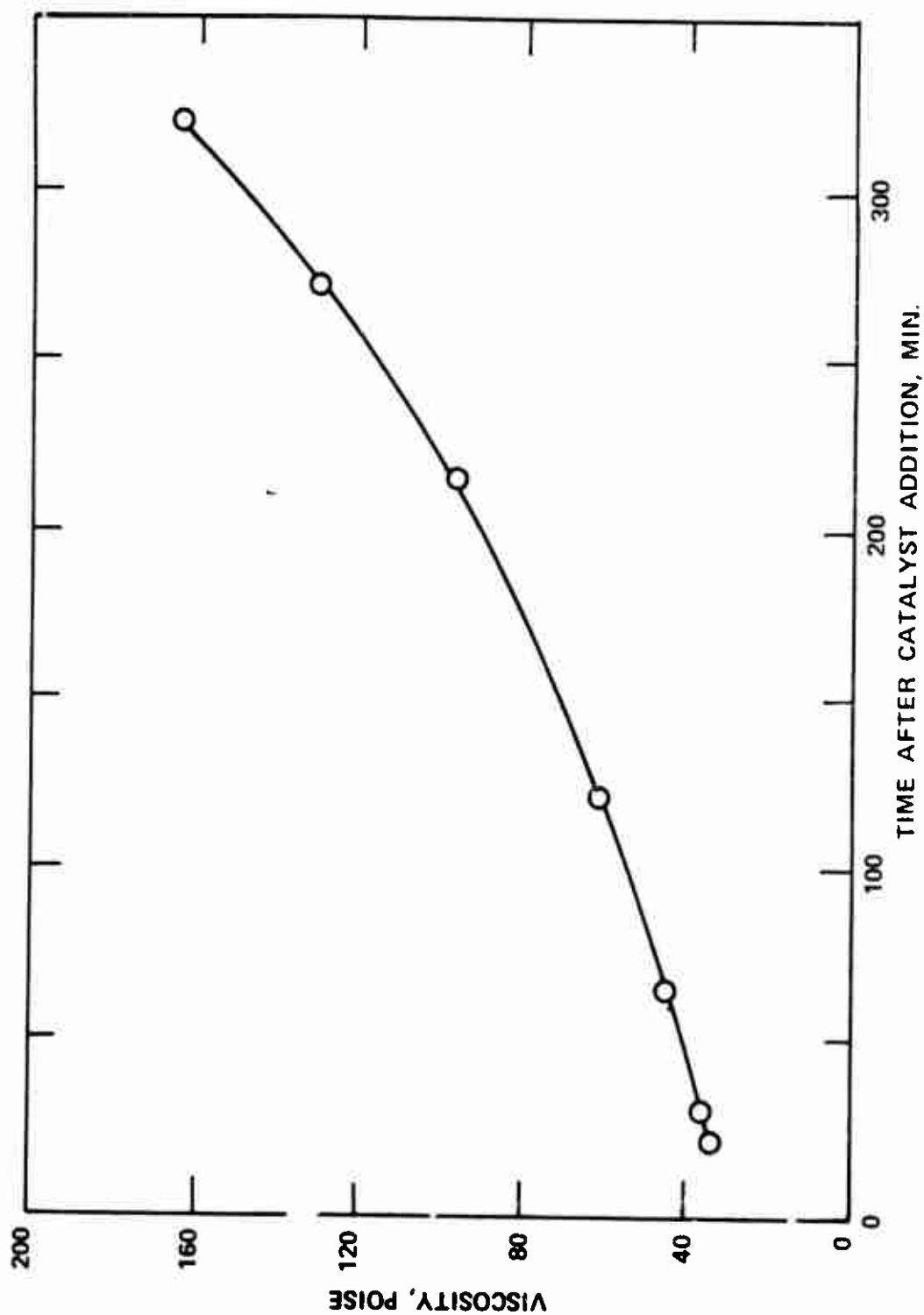Figure 38 - Secant Modulus at 30% Elongation vs. Cure Time for Telagen X196-53

Figure 39 - Viscosity Study of Telagen Binder with 0.4% Chromium Octoate at 26°C

Telagen-epoxide reaction at equal CrOct levels. It was also found that the presence of solids had no effect on the rate at which binders cured and that using equivalent amounts of aziridine and carboxyl (A/C - 1.0) would give a binder which had too high a gel content for use in propellant. One possible explanation for the slow cure is the fact that HX-868 is an acyl aziridine and is subject to rearrangement to form oxazolines. The oxazoline will react with carboxyls but at a slower rate than do the aziridines.

A second set of binders was made in which the CrOct level was varied from 0.4 to 1.0% and the A/C ratio was lowered to 0.8. Figure 40 shows the cure curves for three of the catalyst levels. Cure is not quite complete in 3 weeks even at the 1% CrOct level. Postcure of CTPB propellants cured with HX-868 is well known, for example, the Aerojet Minuteman propellant ANB-3066 (Ref. 7). The differences in strengths between the three binders shown is attributed to a loss of curatives to side reactions at the lower catalyst levels. In order that the cured propellant have as high an amount of the desired crosslinks as possible the catalyst level to be used should be the maximum concentration which gives an acceptable pot life.

A binder viscosity study was carried out which indicated that 1% CrOct should be close to the maximum allowable level due to pot life considerations.

The first Telagen-aziridine propellant which was prepared had an A/C of 0.70 since the second binder gumstock study also gave binders whose gel contents were too high at the high catalyst level.

b. HC-434 gumstocks: Figure 41 is a plot of percent gel content vs. cure time for various HC-434 binder compositions at the two CrOct levels, 0.4 and 0.2%. At the 0.4% catalyst level, the maximum gel content was generally reached within 7 days, while at the lower level cure was not complete at 7 days. At an intermediate cure catalyst level of 0.3% which is not shown on the figure, gel content was still increasing in the 7- to 10-day period. The presence of the various propellant fillers (AP, oxamide, Fe_2O_3, and Al) when 0.4% CrOct was present did not materially alter the gel content achieved by the binder.

An HC-434-aziridine gumstock study was performed prior to propellant manufacturing. Since it was determined in the Telgen case that more CrOct cure catalyst was required to cure the CTPB with aziridine (HX-868) than with epoxides, CrOct levels from 0.9 to 1.5% were tested here. The study was conducted for a period of 93 days and the axiridine-to-carboxyl ratio was also varied in order to determine its effect on cure time.
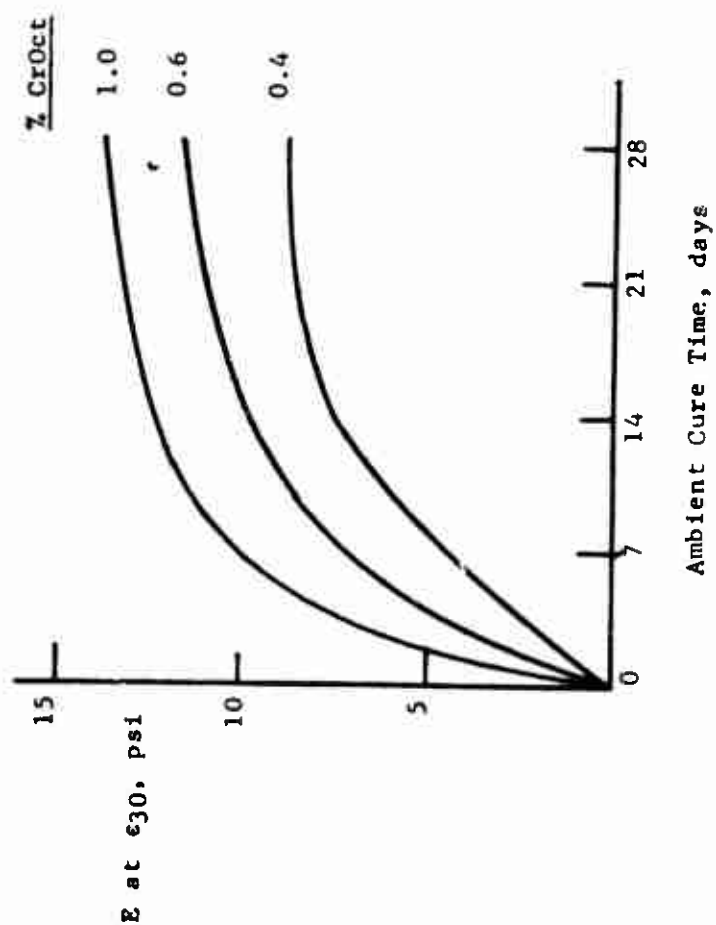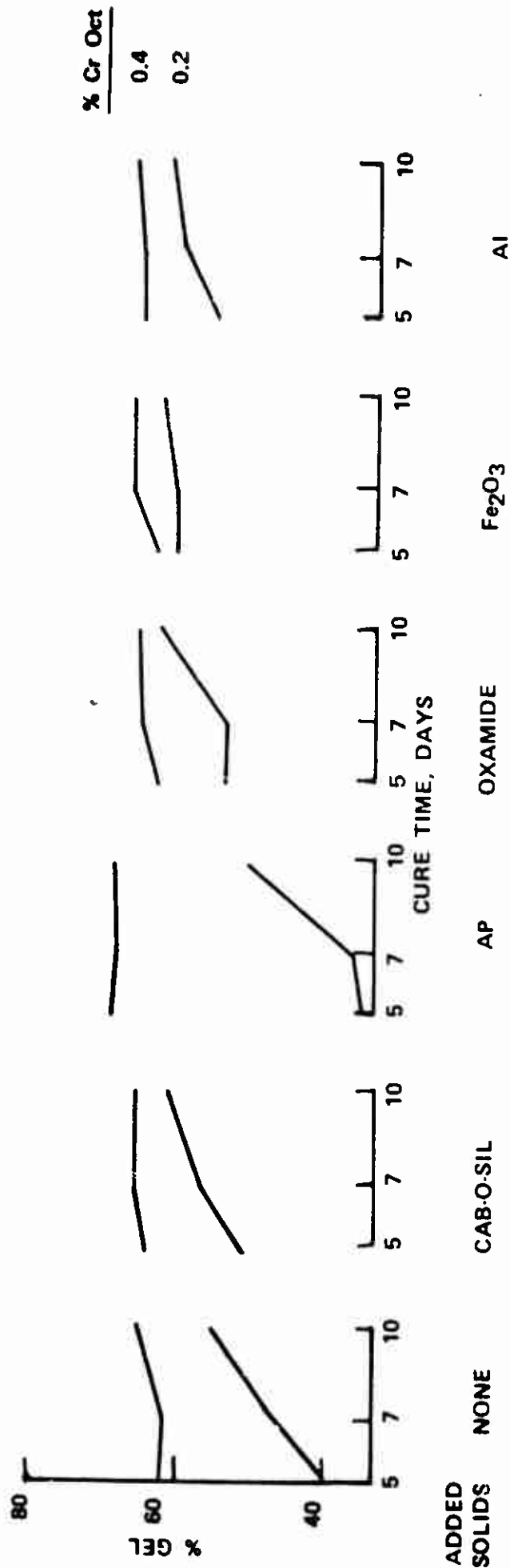
Figure 40 - Secant Modulus at 30% Elongation vs. Cure Time for
Aziridine-Telagen Binders X237-16

Figure 41 - Percent Gel Content vs. Cure Time for HC-434 (X155-92, 99)

Figure 42 presents cure data in terms of secant modulus at 30% elongation vs. ambient cure time. It can be seen that the higher A/C, as well as higher CrOct levels, give the binder a higher modulus and also that the modulus of all four systems was increasing even beyond the 46-day point. Figure 43, which is a plot of percent of final secant modulus vs. cure time, more clearly shows the effect of catalyst level at the two stoichiometries. From Figure 43 it can be seen that cure was faster at the lower stoichiometry, i.e., when carboxyl was in excess, even though the catalyst level was also lower. Therefore, for the fastest possible ambient cure the CrOct level should be the highest value permitted by pot life considerations and the aziridine-to-carboxyl ratio should be the lowest value permitted by the ultimate mechanical properties desired of the propellant.

The cause for slower cure at higher aziridine concentration may be attributed to the aziridine rearrangement reaction provided that the rate of rearrangement is more dependent upon aziridine concentration than is the aziridine-carboxyl reaction. If this is true, more aziridine will rearrange to the oxazoline structure during cure at the higher A/C. Since oxazoline reacts with carboxyl at a lower rate than does the aziridine, a buildup of oxazoline in the propellant will result in very long cure time.

c. _PBAN gumstocks_: PBAN is a terpolymer of butadiene, acrylic acid and acrylonitrile manufactured by American Synthetic Rubber Corporation. This liquid rubber contains 4.8% of the emulsifying agent Ammonyx T, an ammonium salt. An initial PBAN binder gumstock study which contained just the triepoxide and 0.3-0.4% CrOct showed that unfilled binders were cured in 2 weeks at ambient with the higher CrOct level. However, when AP, Fe_2O_3 and Cab-O-Sil, all at the 1% level, were present the binders were not cured enough for mechanical property testing until 20 days of ambient cure. Since these solids were not found to interfere with the cure of the other prepolymer gumstocks this behavior was tentatively attributed to the presence of the Ammonyx T. Amines do react with AP to liberate ammonia which could interfere with cure but ammonia was not detected when AP was added to a sample of Ammonyx T. Later in the program it was determined that the presence of NH_3 does not affect CrOct-catalyzed ambient propellant cure. No satisfactory explanation for the interference of solids in PBAN cure was obtained. Model compound studies were performed at MRI using PBAN or Telagen and neat Ammonyx T, and evidence of a side reaction in the PBAN system was noted. The exact nature of the cure inhibition reaction is not defined.

A second binder gumstock was performed using both di- and tri-epoxide, filler and higher cure catalyst levels. The epoxide-to-carboxyl ratios were unity. The all-diepoxide binders containing up to 2.0% CrOct
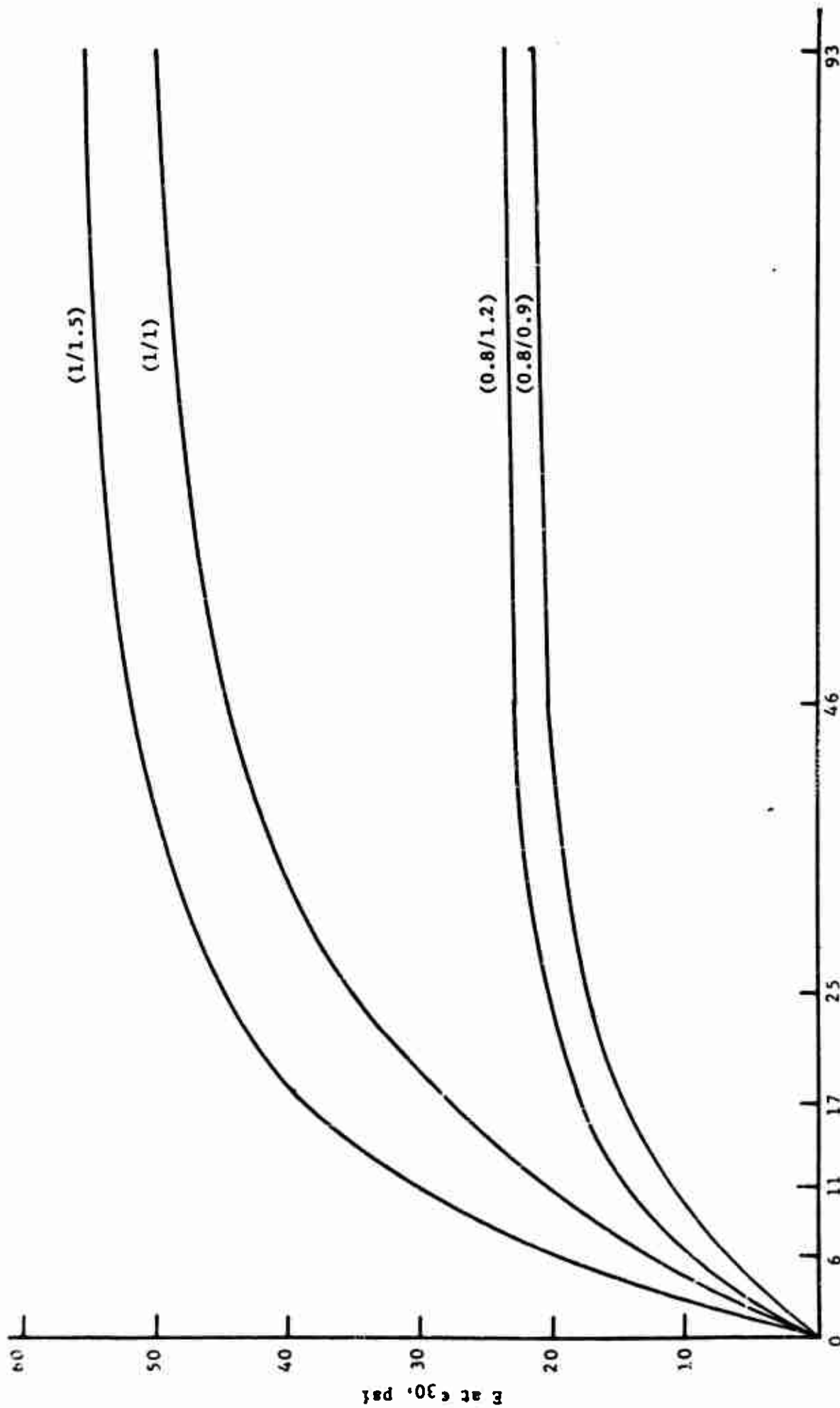
Figure 42 - Secant Modulus vs. Cure Time for HC-434 - HX-868 Binders X248-24 (A/C and % CrOct shown)
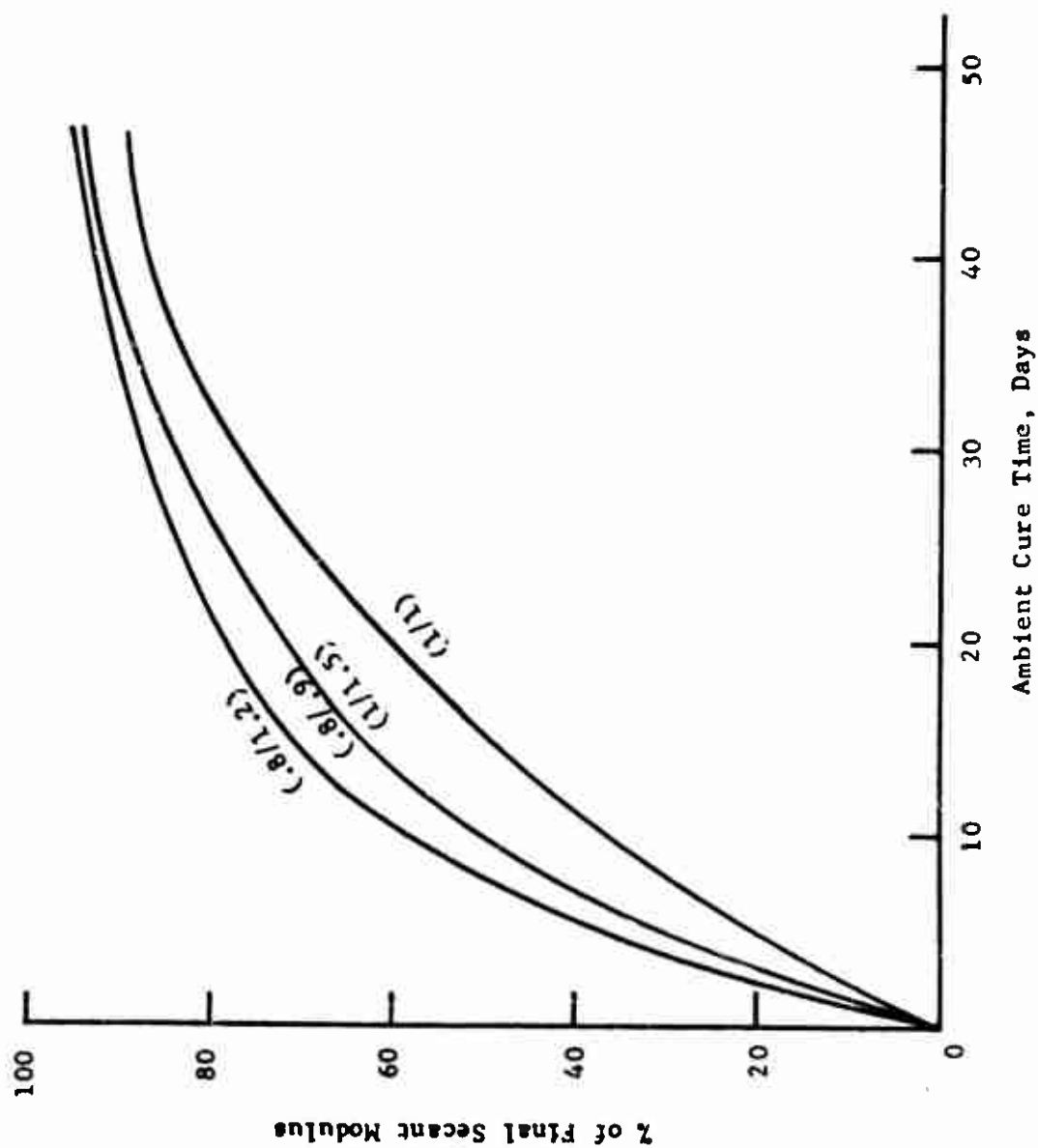
Figure 43 - Percent of Final Secant Modulus vs. Cure Time for Binders
X248-24 HC-434 - HX-868 (A/C % CrOct)

137

failed to cure but those with all-triepoxide cured at a rate only slightly slower than the unfilled binders (of 0.4% catalyst) when 1-2% CrOct was present. A binder viscosity study was performed which indicated that 1.5% CrOct was the maximum concentration of catalyst which would give good pot life. Therefore, the cure inhibition observed in the PBAN-epoxide system relative to the two CTPB prepolymers can be overcome simply by increasing the cacalyst concentration.

Two binder gumstock studies were carried out on the PBAN-aziridine cure system in order to determine the best catalyst level and A/C ratio for ambient cure and good pot life. Propellant solids (1%) were included in all the mixes since it was found that the presence of these solids in the PBAN-epoxide system required a different CrOct cure catalyst concentration than did the unfilled binders. In the first study, the CrOct level was varied from 0.4 to 2.0% of the binder and both 0.8 and 1.0 A/C were used. None of these binders cured well enough in 1 week to obtain mechanical property specimens. In the second study 2%, 3%, 4% and 5% CrOct were used with an A/C of 1.0. The binder with 5% CrOct had a viscosity which indicated that a propellant could be manufactured with high concentration. All gumstocks were very slow to cure and no mechanical property data were obtained. Qualitatively, a cure time of several months at ambient was indicated.

d. EA/AA gumstocks: A fourth prepolymer which was to be studied in this program was the copolymer of ethylacrylate and acrylic acid (EA/AA) synthesized by Celanese Corporation. The prepolymer, which had an acid content of 5.2%, was not very soluble in the plasticizers DOA or IDP but was miscible with either tri-n-butylphosphate (TBP) or triacetin (TA). The TA-prepolymer solution slowly cured with the triepoxide at ambient without any added catalyst. The EA/AA-TBP solution did not have this characteristic but both plasticizers were used in the subsequent binder gumstock cure studies.

In gumstock studies, plasticizer-to-polymer ratios of 1 to 5 were used with the epoxides ERLA-0510, DER-332, ERLA-4221 or UNOX-221, E/C ratios of 0.8 to 3.6, CrOct levels of 0.2-0.4 and AP filler to stimulate homopolymerization of the epoxide when excess epoxide was present. Cured gumstocks had very little strain at maximum stress and problems were anticipated when EA/AA was to be used in the 85.5% solids propellant of this program. A plasticizer-to-polymer ratio of 3 was necessary in order to obtain binders with TBP which had about the same initial viscosity as the CTPB binders at 25°C.

The best gumstock cures were obtained with TBP/EA/AA - DER-332, E/C = 3.6 and 0.4% CrOct. Two 1-lb. propellant mixes were made with DER. In both cases the pot life was very short and end-of-mix viscosity

138

exceeded 160 Kp. After 5 weeks of ambient cure, the propellant was still too soft to cut mechanical property specimens.

It was concluded that propellants based on the EA/AA copolymer were not processable at the normal binder and plasticizer levels used in 85 to 88% solids propellants. The intrinsic viscosity of EA/AA is such that it must be highly plasticized in order for it to be the basis of a processable propellant; yet, enough prepolymer must be present in the propellant so that a sufficient crosslink density is achieved and the grain will be consolidated after curing. The limit of processability of EA/AA propellants is about 20% binder when elevated mix temperature and high aluminum levels are used. Normally, 30% or more binder is used in high-energy EA/AA propellants. The high energy is attained by the use of an energetic plasticizer such as TVOPA. Since the use of explosive plasticizers is beyond the scope of this program, the remaining EA/AA studies were deleted from the program. The funds saved by this deletion were directed to an expanded inveatigation, through the 5-gal. mix of the other three prepolymers of this program.

3. Chromium oleate: A gumstock study of Telagen prepolymer cured with chromium oleate was performed to see if the oleate might offer any advantages over the octoate. The catalyst materials used were prepared by Shepherd Chemical Company and contained 4.7 and 6.0% Cr (theoretical is 6.16, while the MRI tested material was 4.0% Cr). Results, which are given in Figure 44, show that even at the high 0.80% catalyst level, cure is not complete in 15 days with the purer chromium oleate sample. This high catalyst level corresponds to a Cr content equivalent to 0.44% CrOct. Since the Cr oleate appeared to be inferio: to CrOct no further work was performed with the oleate.

4. Chromium 2,6-diisopropyl salicylate: Chromium 2,6-diisopropyl salicylate (CrDIPS) was a cure catalyst recommended and supplied by the Explosives Research and Development Establishment, Waltham Abbey, England. The matrix of Telagen binders was prepared and is shown on the following page. A plot of modulus versus ambient cure time for these binders is shown in Figure 45. The epoxide binders cured with CrDIPS were not strong enough to prepare mechanical property specimens, even when a higher Cr level than the CrOct baseline formulation (0.5% of the binder) was used. In the aziridine case, the CrDIPS sample was weak but tractable. From the figure, it can be seen that both catalysts cure the aziridine binder in 14 days at ambient, but the higher modulus of the CrOct sample indicates a higher degree of crosslinking. Since the low modulus indicates that undesirable side reactions took place (perhaps homopolymerization) CrDIPS would not be recommended as a replacement for CrOct in ambient-cured propellants on the basis of this study.
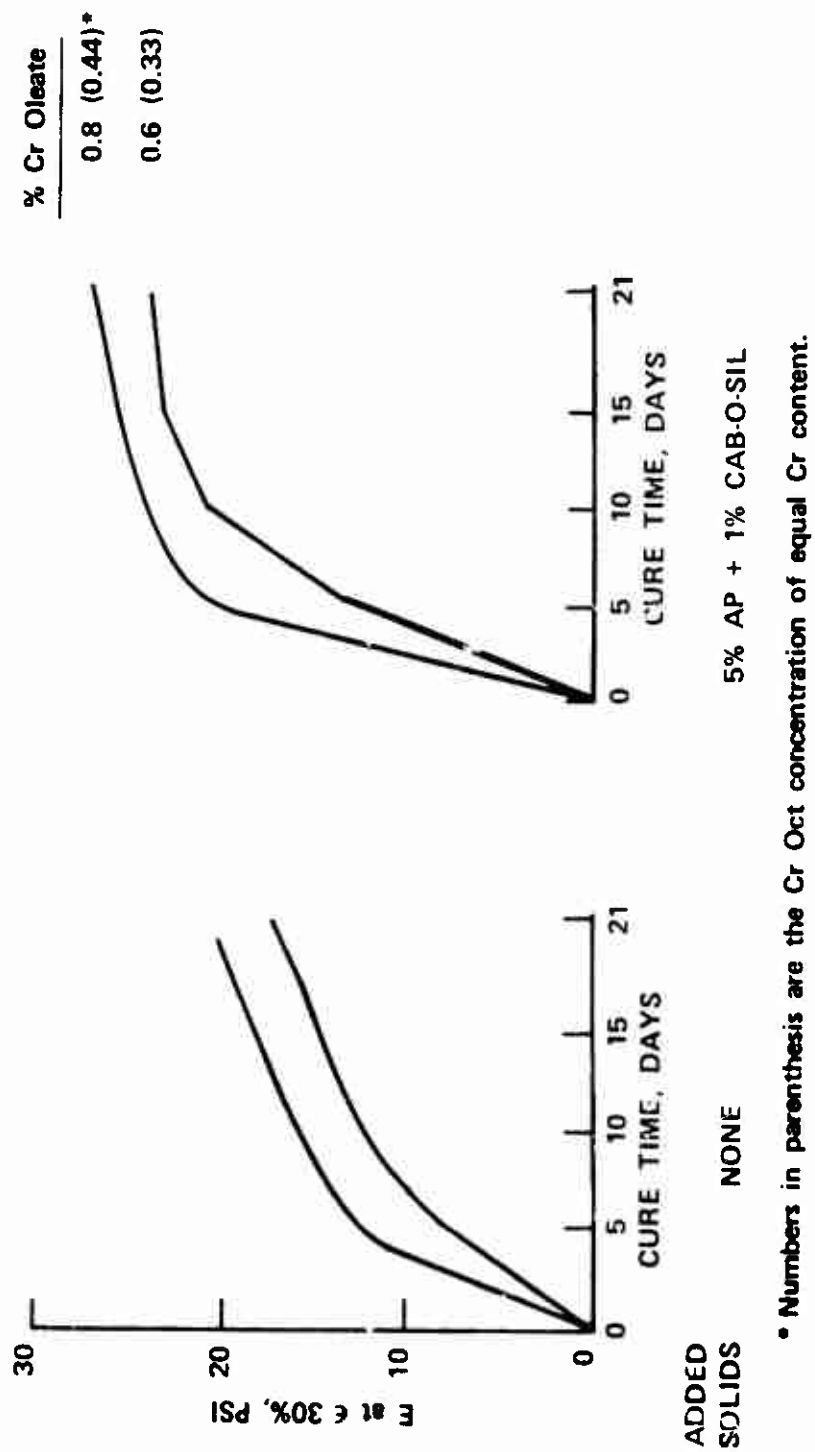
Figure 44 - Secant Modulus at 30% Elongation vs. Cure Time X196-79
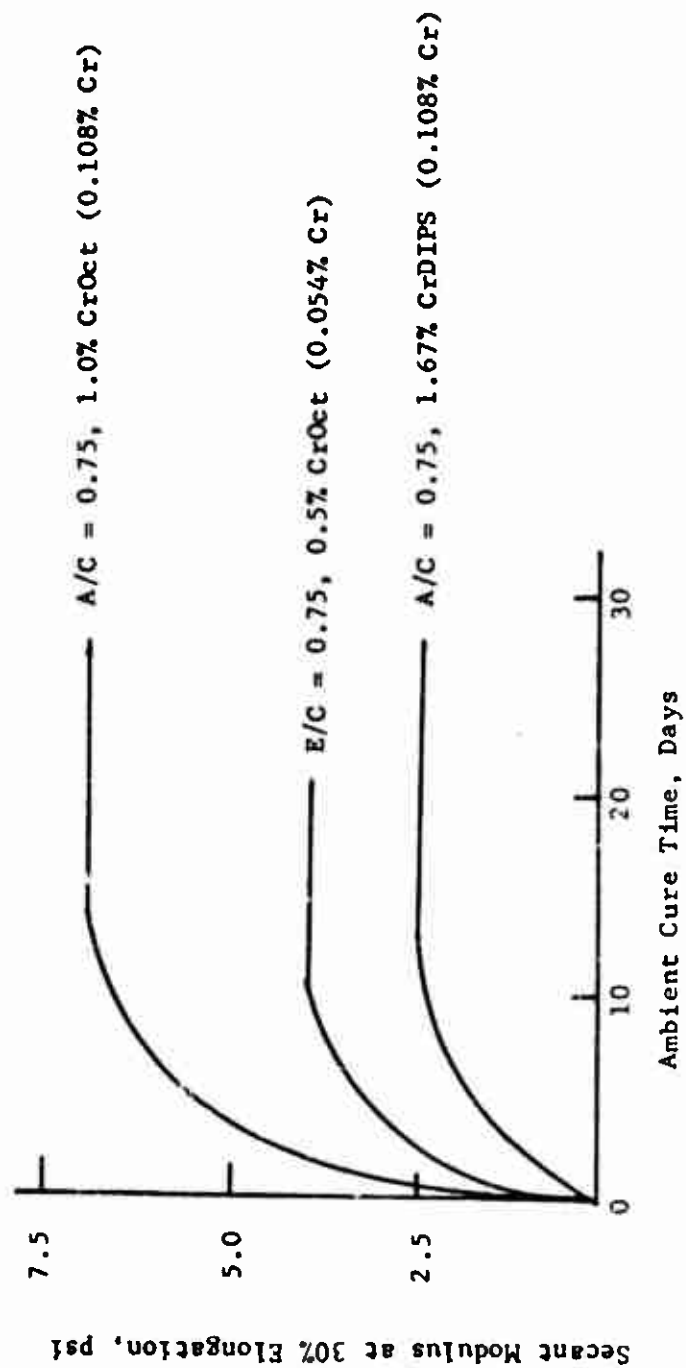
Figure 45 - Modulus vs. Cure Time for Binders X248-49 Telagen-Epoxide or HX-868

141

A 1-lb. propellant mix was prepared with CrDIPS which confirmed
the gumstock results.

AMBIENT CURE OF TELAGEN BINDERS

Curative	% Catalyst	% Cr	Results (see Figure 45)
Epoxide	0.5 CrOct	0.054	Baseline formulation, full cure ~ 15 days
Epoxide	0.83 CrDIPS	0.054	30 day cure too soft to test
Epoxide	0.664 CrDIPS	0.045	30 day cure too soft to test
Epoxide	0.996 CrDIPS	0.065	30 day cure too soft to test
Aziridine	1.0 CrOct	0.108	Baseline formulation, full cure ~ 15 days
Aziridine	1.67 CrDIPS	0.108	Full cure ~ 15 days

X.

SCALE-UP DEMONSTRATION OF CURE CATALYSIS

A. Summary

The CrOct catalyst concentration and curative stoichiometry were optimized for the six propellant binder systems. Catalyst levels and cure times for the six baseline formulations are shown below:

Baseline Propellant Compositions

System	% CrOct in Binder	Cure time, days
Telagen-epoxide	0.50	14
HC-434-epoxide	0.45	14
PBAN-epoxide	1.75	28
Telagen-aziridine	1.00	21
HC-434-aziridine	1.20	21
PBAN-aziridine	5.00	> 150

CrDIPS was shown to be inferior to CrOct as a cure catalyst for these ambient-cured carboxyl propellants.

Water contamination was found to lower propellant tensile strength but did not affect ambient cure time. Water solutions of the contaminants NH_3, $HClO_4$, HNO_3 and HF were also tested in the Telagen-epoxide baseline propellant. Cure times were unchanged with the exception of the HF case in which the cure rate appeared to be increased.

Oxamide shortens the pot life of the Telagen-epoxide baseline propellant. The antioxidant, thiodiphenylamine, consumes curative in these ambient cured propellants to a higher degree than in 140°F-cured propellants. CrOct does act as a surfactant for these propellants.

A surveillance program conducted for 6 months at 75° and 160°F on propellants cured at both ambient temperature and 140°F showed that the ambient-cured propellants aged as well as the heat-cured propellants.

The Telagen-epoxide propellant had the best aging characteristics of the four binder systems examined. Although it was shown that a higher degree of desired ester crosslinks formed during ambient cure than during 140°F cure, there was no evidence that this resulted in improved aging characteristics.

B. Discussion of Results

1. Procedure: Initially, 1-1b. propellant mixes were manufactured with cure catalyst concentrations selected on the basis of the binder gumstock studies. If necessary, further 1-1b. mixes were then made in order to optimize the catalyst level to achieve the best balance between short ambient cure time and adequate (≥ 4 hr.) slurry pot life. Curative stoichiometry would also be varied, if necessary, to obtain good mechanical properties. The optimized propellant was then made on a 10-1b. scale to better define the actual cure characteristics and determine if there were any changes brought about due to scale-up. Having completed this work, a baseline composition was then chosen for each of the six binder systems. The effects of contaminants on cure and the aging characteristics of several of the baseline propellants were then determined.

All propellants had the same basic composition consisting of 14.5 wt. % (27.5 vol. %) binder, 80% AP, 5% aluminum and 0.5% Fe_2O_3. The binders were 70% polymer with catalyst and plasticizer taking up the remaining 30% of the binder phase. The 1-1b. and 10-1b. propellant mixes were manufactured in a 1-quart and 1-gal. Baker-Perkins double verticle planetary mixer, respectively. The 40-1b. mixes were prepared in a 5-gal. Day mixer. Mixer temperature was 25°C in all cases. The solids were added incrementally and the catalyst was added as a THF solution 40 min. before the end of the mix cycle. Viscosities were measured on a Haake rotoviscometer and the values reported here are at a shear rate of 0.41 sec.$^{-1}$. Cure time was followed by either gel content analysis or mechanical property measurements. Propellant mechanical properties were measured on Type II JANAF tensile specimens using an Instron tester and a strain rate of 0.74 in/in/min. Since CrOct acts as a surfactant for these propellants, propellant processing was aided. Because of its superior cure catalyzing efficiency, CrOct was choosen as the catalyst for all the baseline propellants.

2. Selection of baseline propellants:

a. Telagen-epoxide propellant: The first propellants processed and cured at ambient temperature (75° ± 5°F) in this program contained the Telagen-epoxide binder, cured with CrOct. All propellants were mixed, cast and post-evacuated without difficulty at ambient temperature. A

144

listing of the Telagen-epoxide 1-lb. mixes is given in Table XXXVII. Initially, 0.37% CrOct in the binder was tested buy later it was determined that as much as 0.5% catalyst could be used and still maintain a good pot life.

It was predicted by the gumstock study that cure of Mix No. X196-87 with 0.40% CrOct should be complete within 8 days. The modulus values for the propellant, which are shown in Figure 46, confirm this. The strain at maximum stress values and tensile data were less precise but indicated that cure was still progressing at a measurable rate beyond the 8-day period.

In subsequent propellant mixes it was determined that a mixture of di- and triepoxides should be used in order to improve the cured mechanical properties and that 0.5% CrOct in the binder was necessary to insure a 2-week ambient temperature cure. The X237-25 formulation was selected as the Telagen-epoxide baseline. A 10-lb. mix (X237-26) of the baseline was prepared which defined and confirmed the 2-week cure time (see Figure 47).

The purpose for using the 10-lb. grains in addition to the 1-lb. grains was to provide many more mechanical property specimens (1/4-in. thick by 5-in. long JANAF dogbones) for testing so that the cure cure-time curve could be unambiguously defined. The baseline X237-26 had a 2-week cure time, since the mechanical properties did not change beyond 2 weeks at ambient or after heating the propellant for 3 days at 60°C. The propellant mold was disassembled after 6 days of cure and the grain was quite strong when properties were first measured. The average mechanical properties of five specimens after 9 days of cure was 320 psi modulus, 102 psi tensile strength and 48% strain at maximum stress. Processing pot life was adequate with the 0.5% CrOct cure catalyst present in the binder phase. Therefore, no unusual problems are anticipated if motors were to be made of this propellant. Mechanical property vs. time results show that cores can be pulled in 1-2 weeks after casting.

Propellant X237-20 containing 0.4% CrOct (in the binder) was also prepared on a 10-lb. scale. The grain, which is pictured in Figure 48, was cured well enough after 8 days to be removed from the mold. Mechanical properties (see Figure 49) did not change after 20 days of cure at ambient, but cure was not complete in 20 days because exposing the propellant to 3 days cure of 60°C after 32 days at ambient gives a significantly stronger propellant grain.

145

TABLE XXXVII

TELAGEN-EPOXIDE PROPELLANTS[a]

Mix No.	% CrOct	Epoxy CO_2H	di/tri Epoxy	Slurry Visc. Kp Time (Hr)	Cure Time (Days)	Mechanical Properties at[a] 77°F, 0.74 min^{-1} Modulus (psi)	Strength (psi)	Strain at Max. Stress (%)
X196-70	0.37	1.00	tri	-	-	1,730	133	9.2
X196-72	0.40	1.00	tri	11 at 5	-	1,800	133	9.4
X196-74	0.40	0.80	tri	15 at 1 15.6 at 1.5	≥ 21	670	118	24.1
X196-87	0.40	0.75	tri	12 at 1 19 at 3	8	510	112	29.6
X222-2	0.37	0.86	0.50	20 at 1 26 at 4	14	860	116	19
X222-12	0.43	0.75	tri	-	14	630	138	31
X222-16	0.40	0.75	0.50	10 at 1 11 at 2	19	490	111	31
X222-55	0.40	0.70	0.50	12 at 1 13 at 2	≤ 33	430	87	25
X237-15	0.40	0.75	0.75	16 at 1 18 at 3	≤ 23	480	120	37
X237-25[b]	0.50	0.75	0.82	11 at 1 12 at 4.5	14	420	110	37
X237-26[b]	0.50	0.75	0.82	17 at 1 23 at 2.5	17	390	116	44
X237-71[b]	0.50	0.75	0.82	9 at 1 12 at 4	14	390	113	43

[a] Propellant composition is 32% 200 μ AP, 24% 130 μ AP, 24% 11 μ AP, 5% H-10 Al, 0.5% Fe_2O_3, and 14.5% binder. The binder is 70% polymer and 30% IDP plasticizer and cure catalyst.

[b] Baseline formulation on 1-lb. (X237-25), 10-lb. (X237-26) and 40-lb. (X237-71) scale.
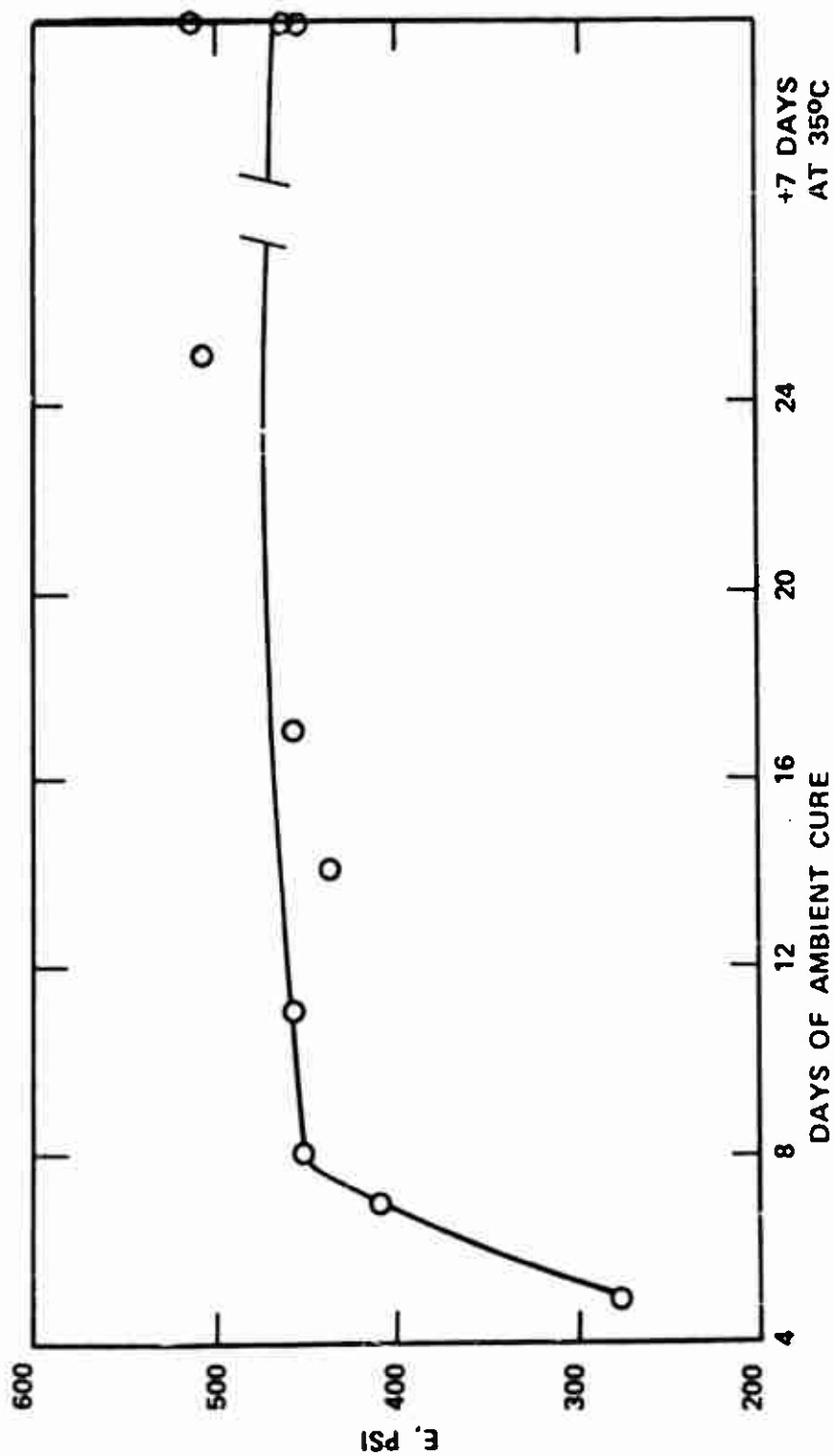
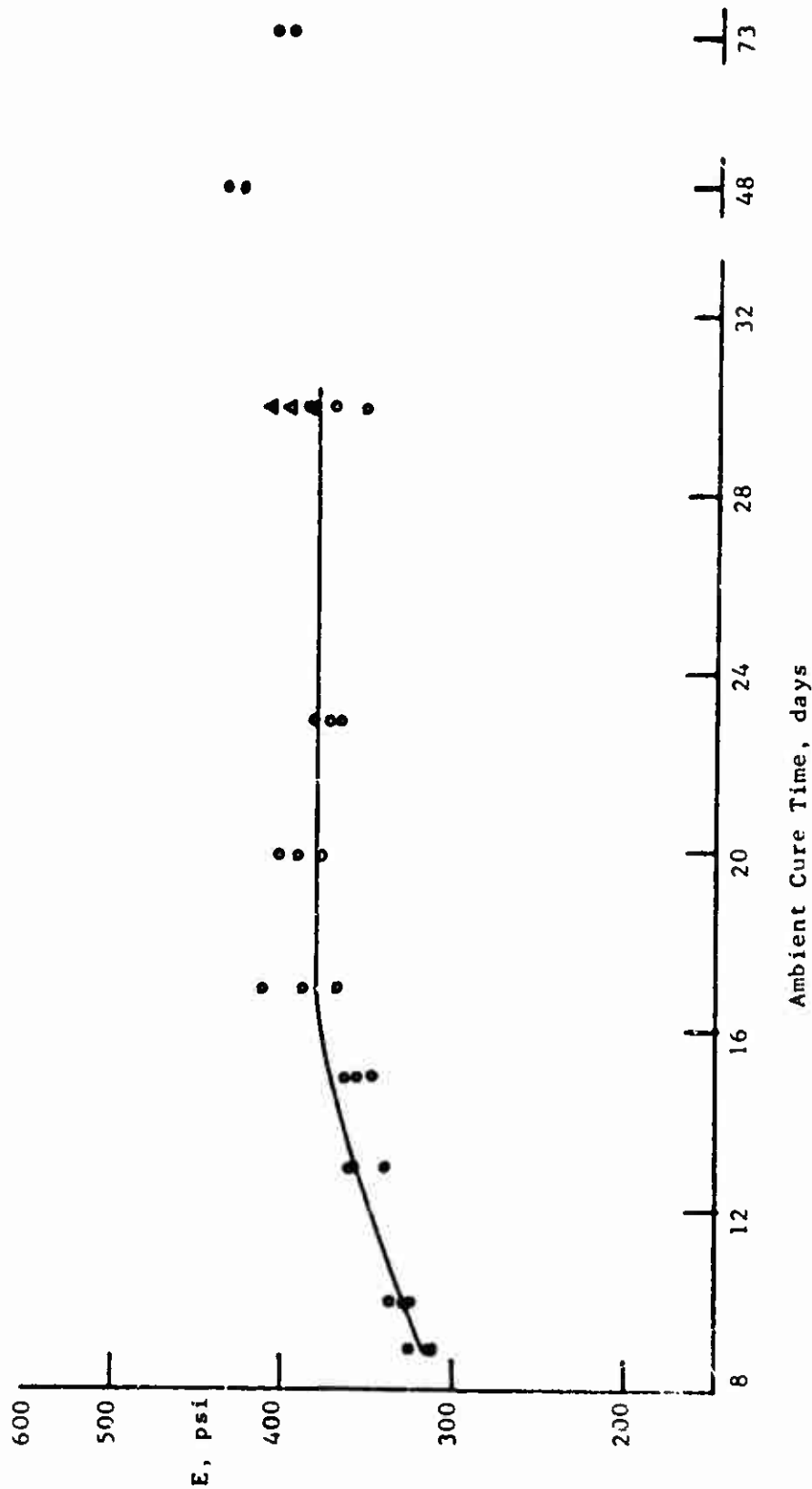Figure 46 - Modulus vs. Cure Time for Propellant X196-87 Containing 0.37% CrOct in the Binder

Figure 47 - Modulus vs. Cure Time for Propellant X237-26 (Telagen, di/tri = 0.82, E/C - 0.75, 0.5% CrOct-Telagen-Epoxide Baseline)

▲ includes 3 days at 60°C
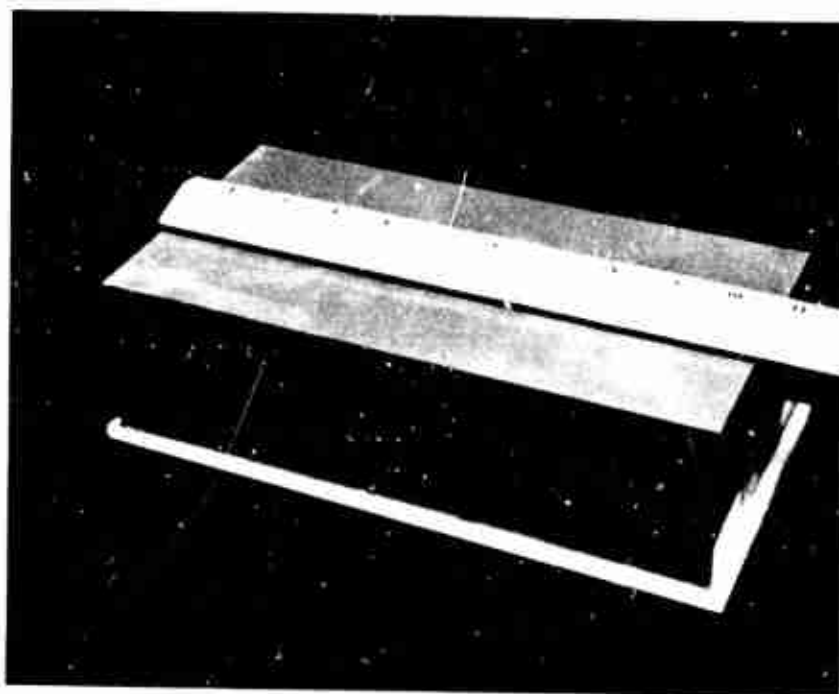
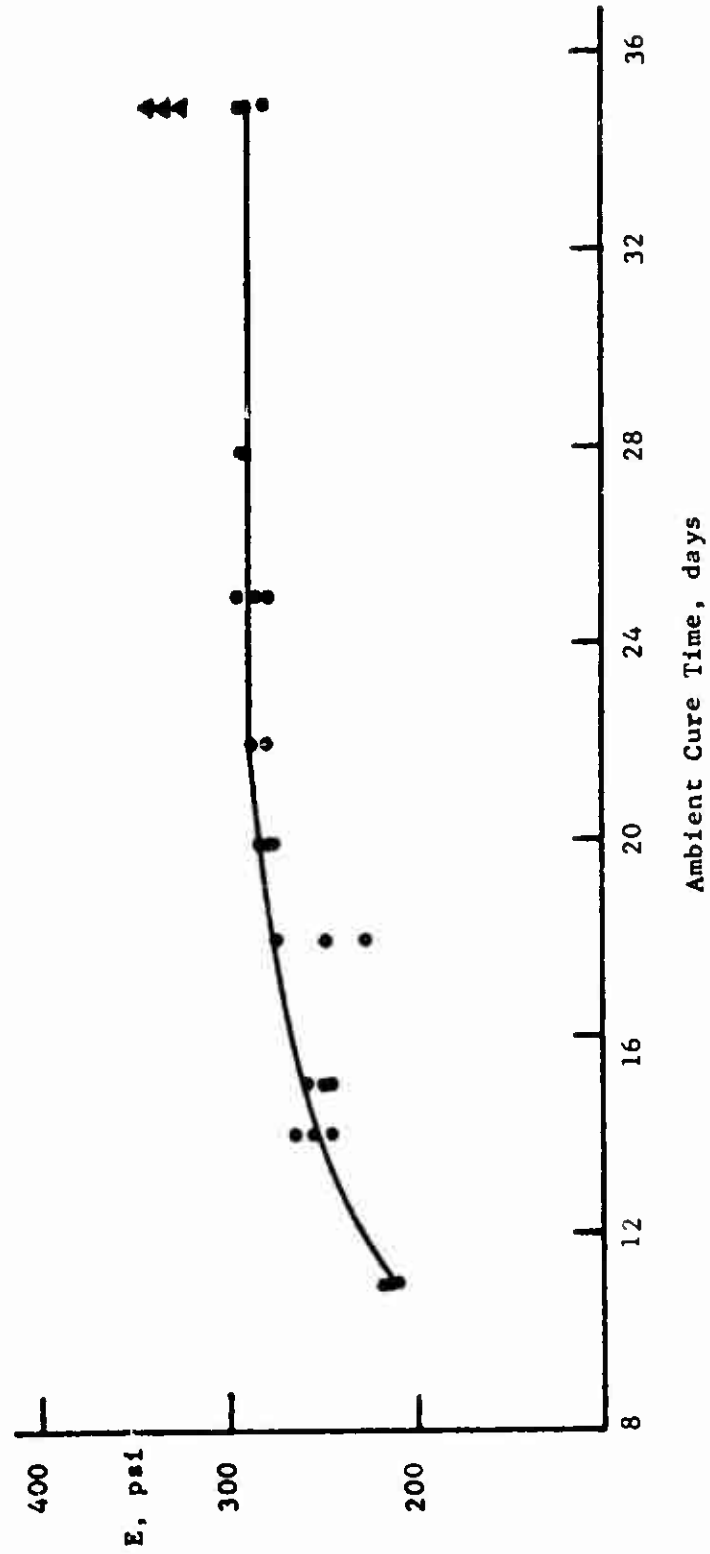Figure 48 - Ten-Pound Telagen Grain Cured 8 Days at 75°F

Figure 49 - Modulus vs. Cure Time for Propellan' X237-20 (Telagen, di/tri = 0.75, E/C = 0.75, 0.4% CrOct

150

The baseline propellant X237-26 (Figure 47) may have increased in strangth slightly after heating for 3 days at 60°C. However, if this was the case, a small degree of post-cure is no problem since the cure was complete enough after 1 week so that a propellant motor could be disassembled and shipped. The minor degree of cure which would take place in the propellant subsequent to this could easily be predicted and would not alter the reliability of the motor. The surveillance of the baseline propellants, discussed in the next section, has as its objective, the determination of post-cure aging characteristics. It was determined that the baseline ages in a similar fashion to 140°F-cured Telagen-epoxide propellant.

b. HC-434-Epoxide propellant: A propellant ambient cure study, similar to the Telagen study, was performed using the HC-434 prepolymer. A summary of the results obtained is tabulated in Table XXXVII. Early 1-lb. mixes indicated that CrOct was an efficient cure catalyst at the 0.40% level (based on binder) but a higher level might be more desirable. E/C of 0.75 coupled with a di/tri epoxide ratio of 0.50 gave good mechanical properties. Viscosity of HC-434 propellants is higher than Telagen propellants. The modulus vs. ambient cure time for propellant X237-21, a 10-lb. casting, is given in Figure 50. The results are quite similar to those obtained for the Telagen grain X237-20, Figure 49. Ambient cure appeared to be complete in 24 days but further cure took place when 31-day old propellant was subjected to 3 days of 60°C. The 10-lb. batch of X237-27, which contained 0.50% CrOct in the binder, was quite viscous and due, presumably to poor dispersion of the curatives, the propellant's homogeniety was very poor. It appears that a 0.45% CrOct level, such as that used in the 1-lb. mix X237-10, would give a better balance between processability and minimum ambient cure time. Mechanical property data for propellant X237-10 are given in Figure 51.

A 10-lb. propellant mix (X237-49) was made with this intermediate concentration (0.45% of the binder) of CrOct cure catalyst. The cure was complete in 2 weeks at 75°F. Mechanical properties remained constant for the remainder of the 46-day period of the study (see Figure 52). However, when the ambient cured propellant was subjected to a week at 60°C, the modulus and strength dropped slightly. This composition was therefore selected as the HC-434-epoxide baseline formulation.

End-of-mix viscosities for the 10-lb. mix (X237-49) and later for the 40-lb. mix (X233-81, see below) were 15 and 16 Kp, respectively, compared to 21 Kp for the 1-lb. (X237-10) propellant mix. This lower mix viscosity for the larger mixes was found to he a general occurrence in this program. The 10-lb. mix was softer than the baseline made on either the 1- or 40-lb. scale; however, this was not a general occurrence and is considered to be due to a small formulation error rather than poor reproducibility of cure.

151

TABLE XXXVIII

AMBIENT CURED HC-434 PROPELLANTS

Notebook No.	% CrOct	Epoxide Carboxyl	di/tri Epoxide	End of Mix Visc. at 26°C (Kp)	Visc. Kp/Time (Hr.)	Time Max. Mod. (Days at 26°C)	Physical Properties at 77°F, 0.74 min^{-1} Modulus (psi)	Strength (psi)	Strain at Max. Stress (%)	Remarks
X196-93	0.40	0.80	tri	24	-	14	920	119	17	
X222-15	0.40	0.75	0.50	16.5	4/5	12	470	131	43	
X222-33	0.40	0.75	0.50	29	26/3	> 22	270	69	41	0.5% TDPA
X222-40	0.40	0.75	0.50	15	12/5	≥ 23	420	111	37	
X222-41	0.40	0.75	0.50	> 50	- -	> 34	206	48	44	0.5% TDPA
X222-61	0.40	0.75	0.50	15	- -	≤ 19	450	120	39	
X222-70	0.40	0.826	0.44	24	16/5	≤ 17	860	147	28	0.5% TDPA
X222-95	0.45	0.75	0.50	26	30/4.5	≤ 15	640	154	36	
X237-10[a/]	0.45	0.75	0.50	21	27/3.5	12	620	126	32	
X237-21	0.40	0.75	0.50	-	31/2.5	-	460	104	33	
X237-27	0.50	0.75	0.50	High	-	-	700	150	35	
X237-49[a/]	0.45	0.75	0.50	15	11/4	14	350	119	49	
X237-81[a/]	0.45	0.75	0.50	16	15/3	14	690	146	41	

a/ Baseline formulation on 1-lb. (X237-10), 10-lb. (X237-49) and 40-lb. (X237-81) scale.

152

▲ includes 3 days at 60°C

E, psi
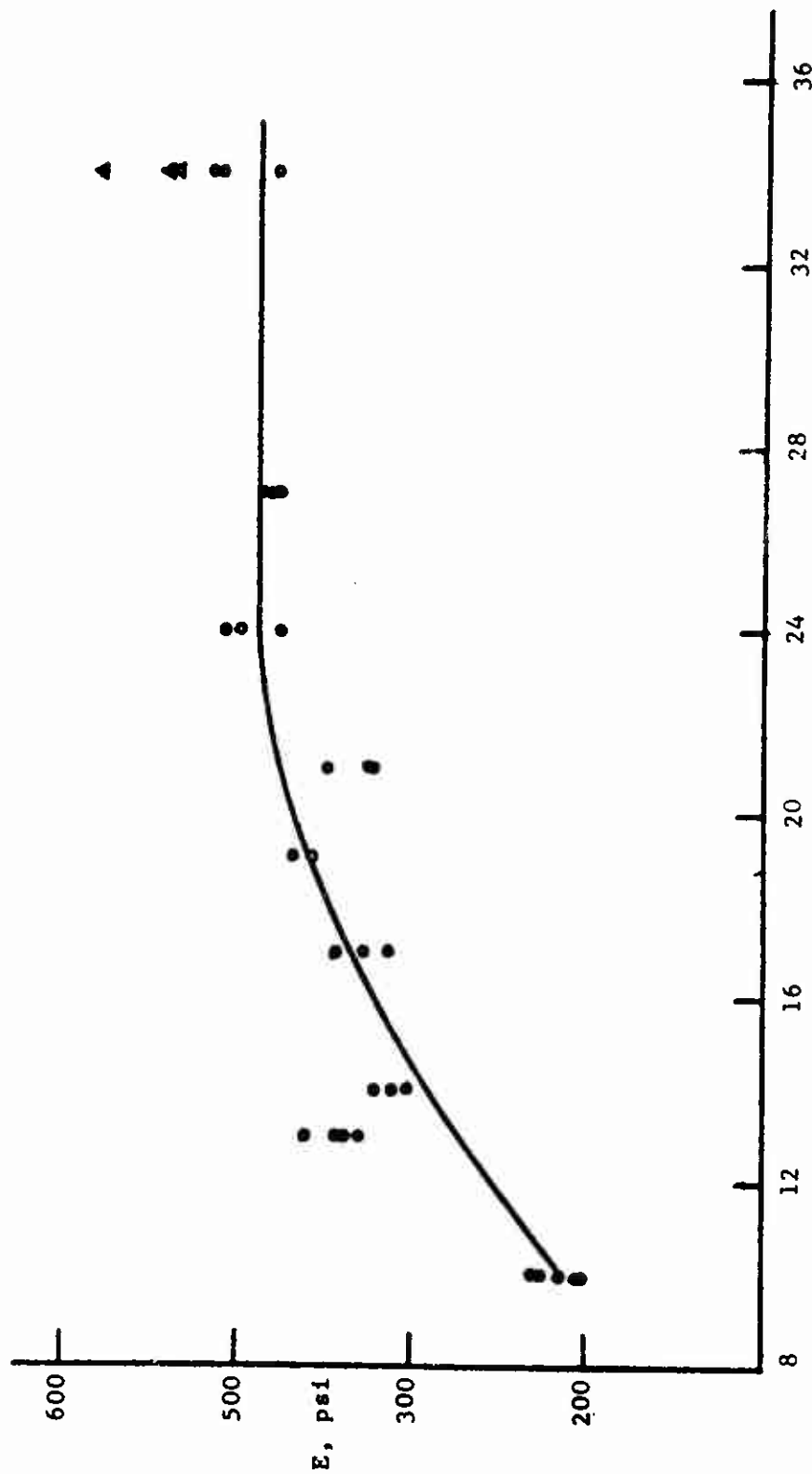
Ambient Cure Time, days

Figure 50 - Modulus vs. Cure Time for Propellant X237-21 (HC-434, di/tri = 0.50, E/C = 0.75, 0.4% CrOct)
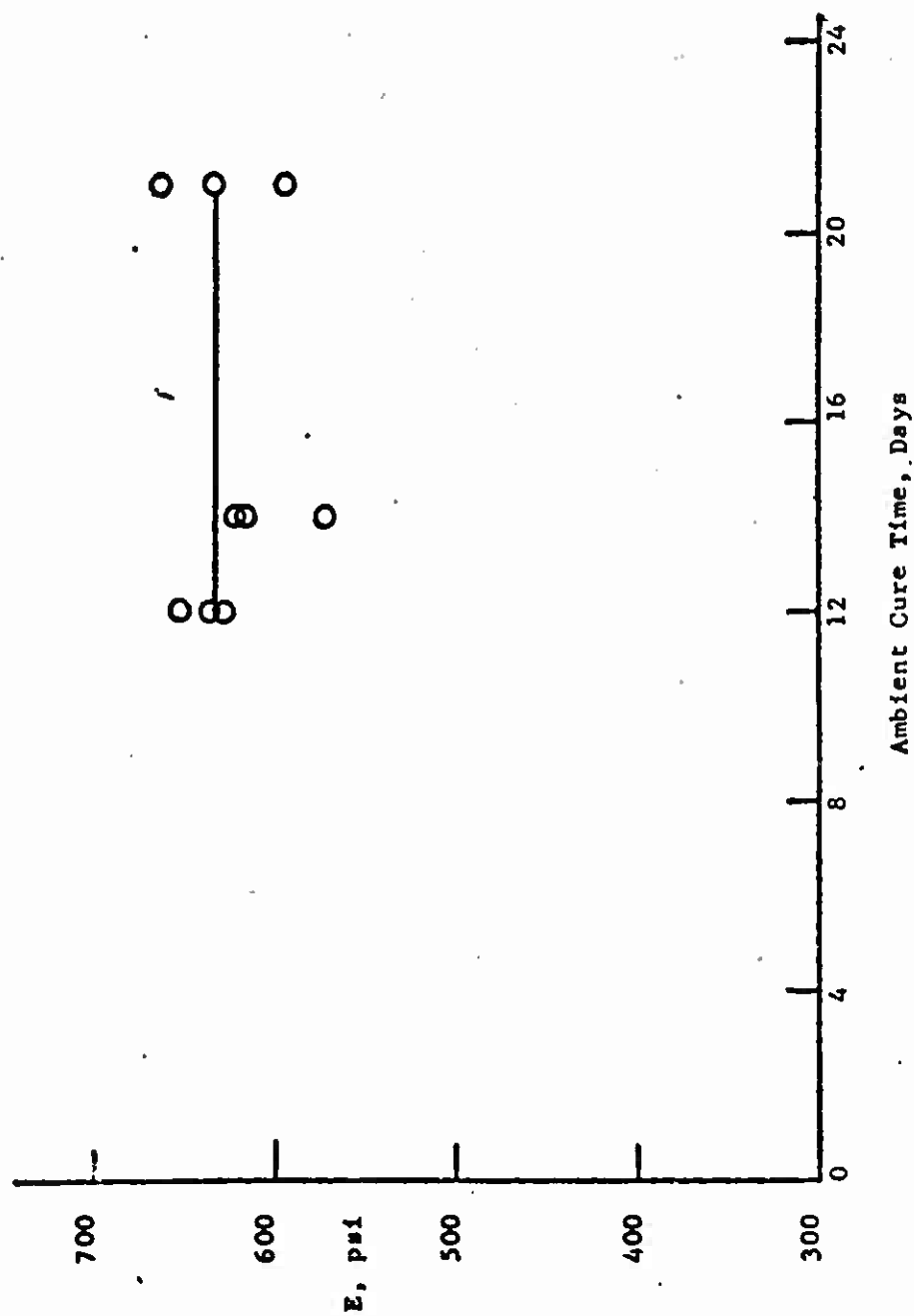
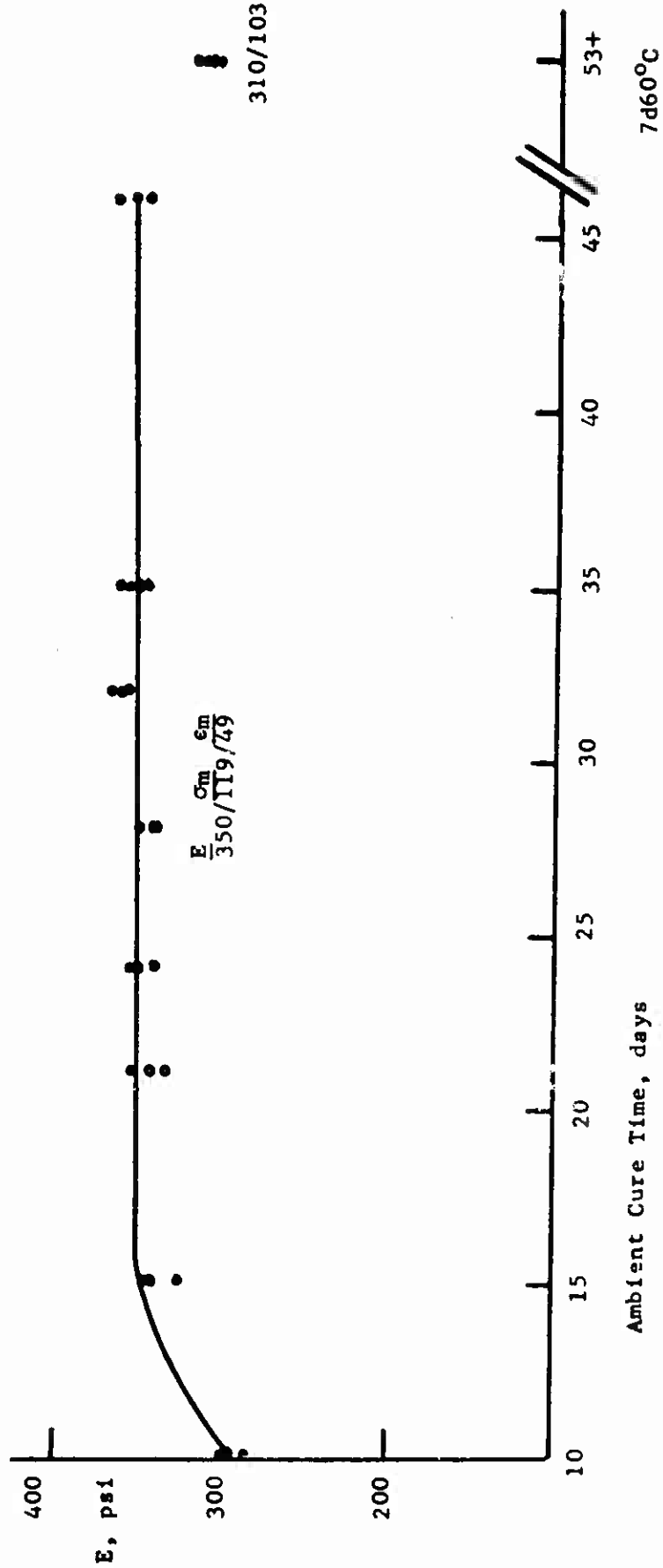Figure 51 - One-Pound HC-434 Mix X237-10 (E/C, = 0.75, di/tri = 0.50, 0.45% CrOct)

154

Figure 52 - Modulus vs. Cure Time for Propellant X237-49 (HC-434, di/tri = 0.50, E/C = 0.75, CrOct = 0.45%)

c. <u>PBAN-epoxide propellant</u>: The terpolymer polybutadiene, acrylic acid and acrylonitrile (PBAN) was found in the Phase III gumstock studies to require considerably more CrOct cure catalyst to cure with epoxides than did the two CTPB prepolymers. This was true only when propellant solids were present; cure of unfilled binder was similar to that of the CTPB's. Presence of the emulsifying agent, Ammonyx T in the PBAN, was suspected of being the cause since this was the only known new constituent of the system. Ammonyx T, an amine salt, could interact with AP in the propellant environment to cause a reduction in curative concentration.

Several PBAN-epoxide propellants were prepared and are given in Table XXXIX. The first 1-lb. mix (X237-46) contained 1.50% CrOct in the binder and had an acceptable pot life (Figure 53) but long cure time (see Figure 54). When the CrOct concentration was increased to 1.75% of the binder (X237-79), the pot life was too short (viscosity 48 Kp in 4 hr.) but cure was complete in 12 days with properties of 500/81/24 (modulus/tensile strength/elongation). Since other propellants had lower mix viscosities when they were scaled-up, it was decided to use 1.75% CrOct in the binder for a 10-lb. PBAN-epoxide mix. This propellant (X237-94) cast well and had a viscosity of only 18 Kp 4 hr. after catalyst addition.

The 1-lb. mix cured faster than did the 10-lb. casting (see Figure 55). Although completion of cure for X237-94 was 4 weeks or longer, this composition was selected as the baseline for surveillance.

d. <u>Telagen-aziridine propellant</u>: The Telagen-aziridine binder gumstock study found that 1% CrOct cure catalyst was probably the maximum permissible level due to pot life considerations and that an A/C of 0.70 should give good mechanical properties.

Propellant X237-52 was prepared with 1.0% CrOct (in the binder) and the viscosity curve is given in Figure 53. The viscosity of 31 Kp at 4 hr. was within the program limit of 35 Kp. The curve time was not well defined by this 1-lb. mix but the catalyst level and A/C ratio appeared optimum. Therefore, 10-lb. mix X237-78 was prepared with the same composition and cure data as shown in Figure 56. It appeared that the propellant was fully cured in 4 weeks or less at ambient. Mechanical properties remained constant through 52 days at ambient but propellant which was then subjected to 7 days at 60°C did cure further. Properties at 52 days at ambient were 510/104/31 and after 59 days at ambient plus 7 days at 60°C were 650/128/28. This indicates that either the cure reaction was not complete during the ambient phase of cure or side reactions are causing an increase in gel content. A comprehensive study of aging properties of this propellant were performed in the surveillance program.

156

TABLE XXXIX

PBAN-EPOXIDE PROPELLANTS

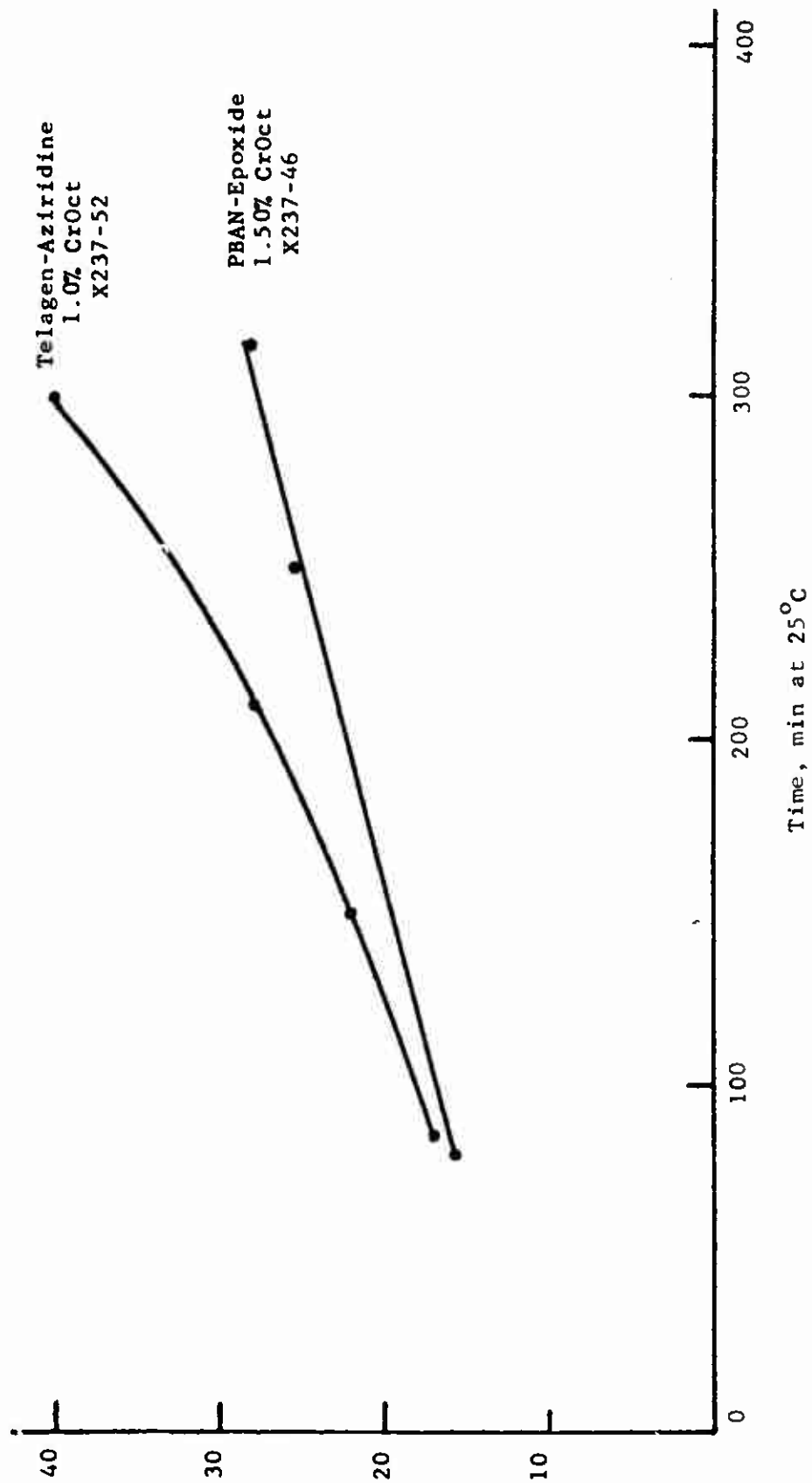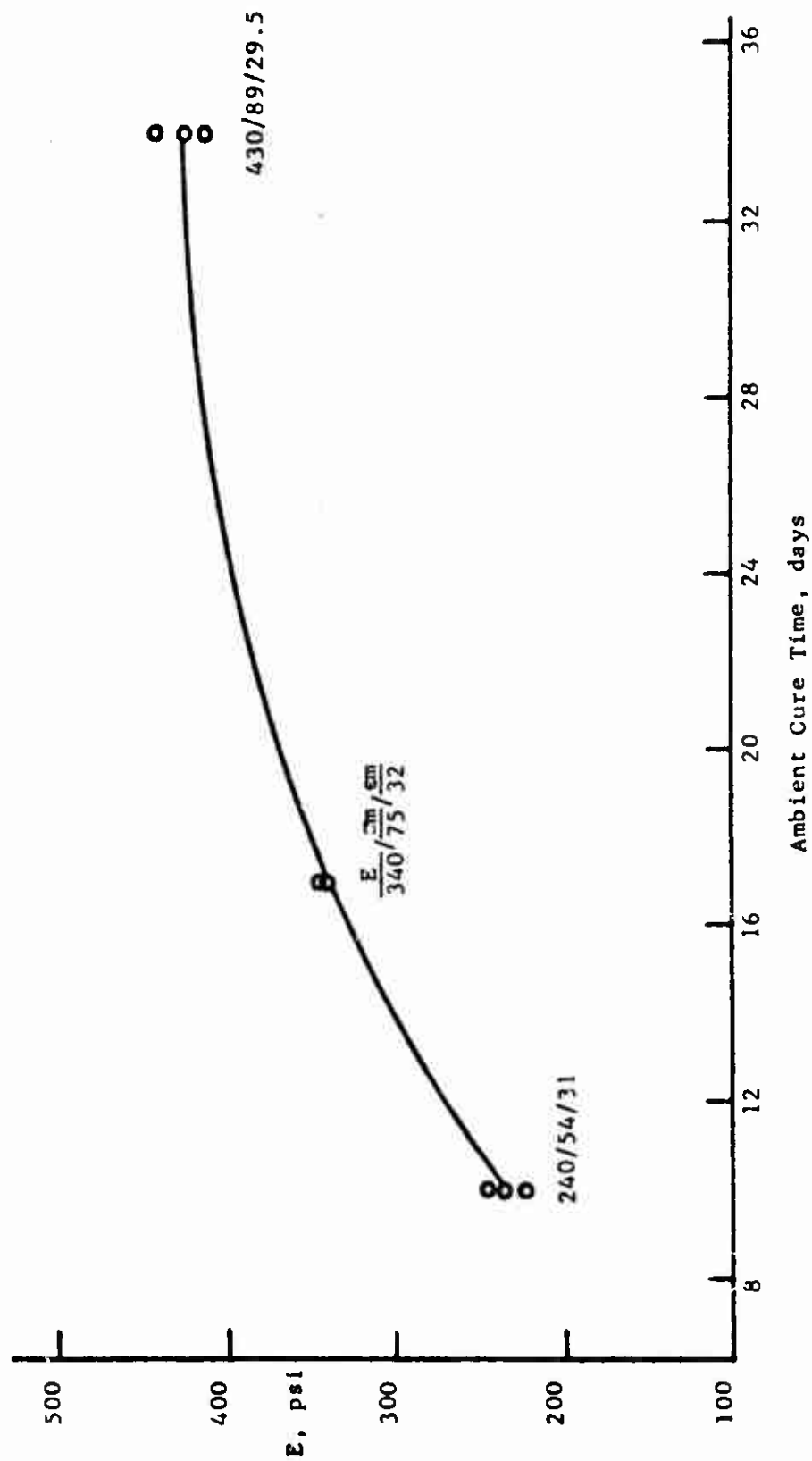| Mix No.	% CrOct	Epoxide Carboxyl	di/tri Epoxide	End of Mix Visc. at 26°C (Kp)	Visc. Kp/Time (Hr.)	Time to Max. Mod. (Days at 26°C)	Physical Properties at 77°F, 0.74 min^{-1}		
							Modulus (psi)	Strength (psi)	Strain at Max. Stress (%)
X237-46	1.50	1.0	tri	16	28/5	34	430	89	30
X237-79	1.75	1.0	tri	21	48/4	12	500	88	24
X237-94	1.75	1.0	tri	12	18/4	28	500	95	31
X248-21	1.75	1.0	tri	-	-	28	400	78	31

157

Figure 53 - Propellant Viscosity vs. Time

Figure 54 - Modulus vs. Cure Time for Propellant X237-46 (PBAN-Triepoxide, E/C = 1, 1.5% CrOct)
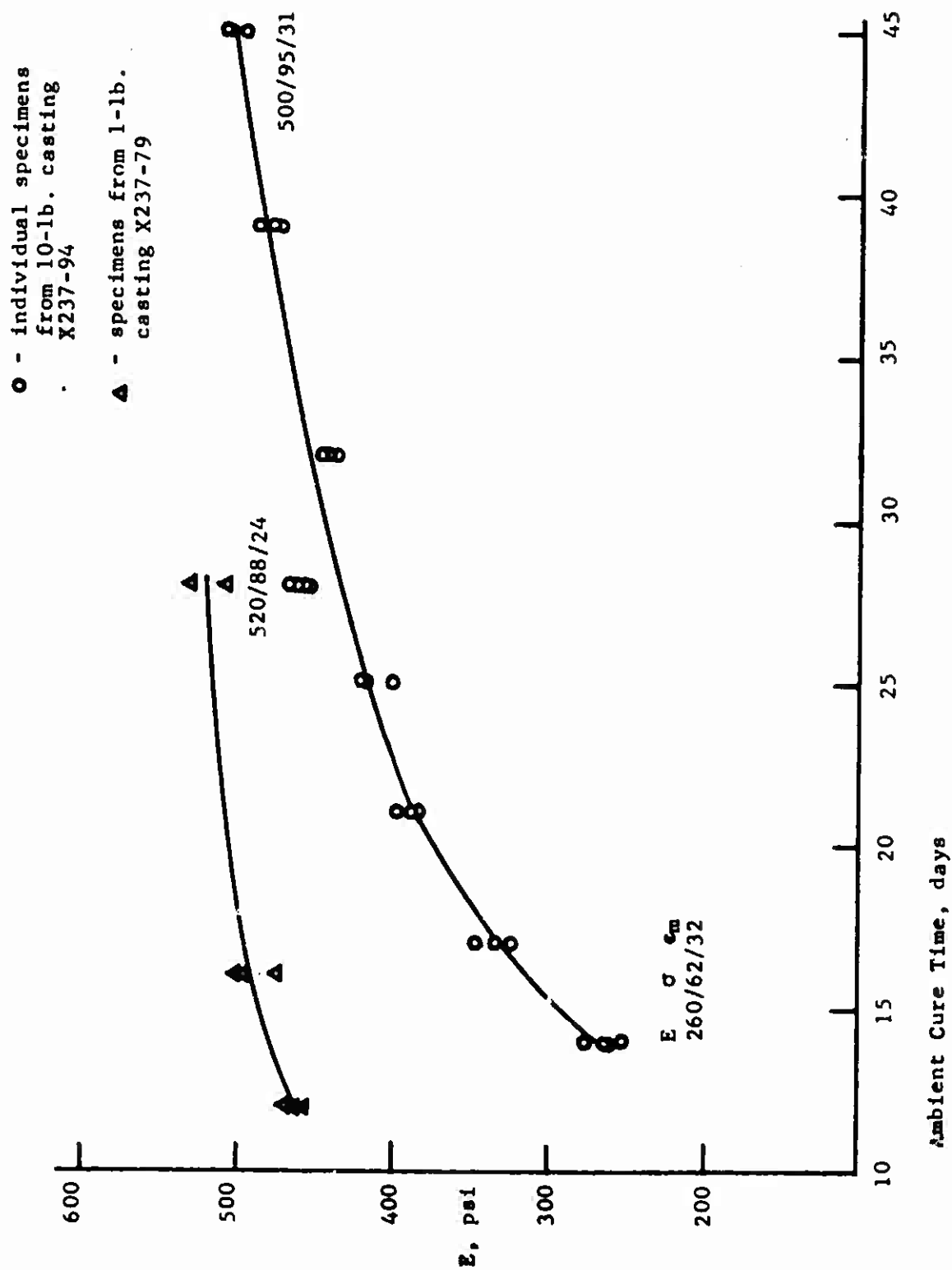
159

Figure 55 - Modulus vs. Cure Time for Propellants X237-94 and -79 (PBAN-Triepoxide, E/C = 1.0, CrOct = 1.75)
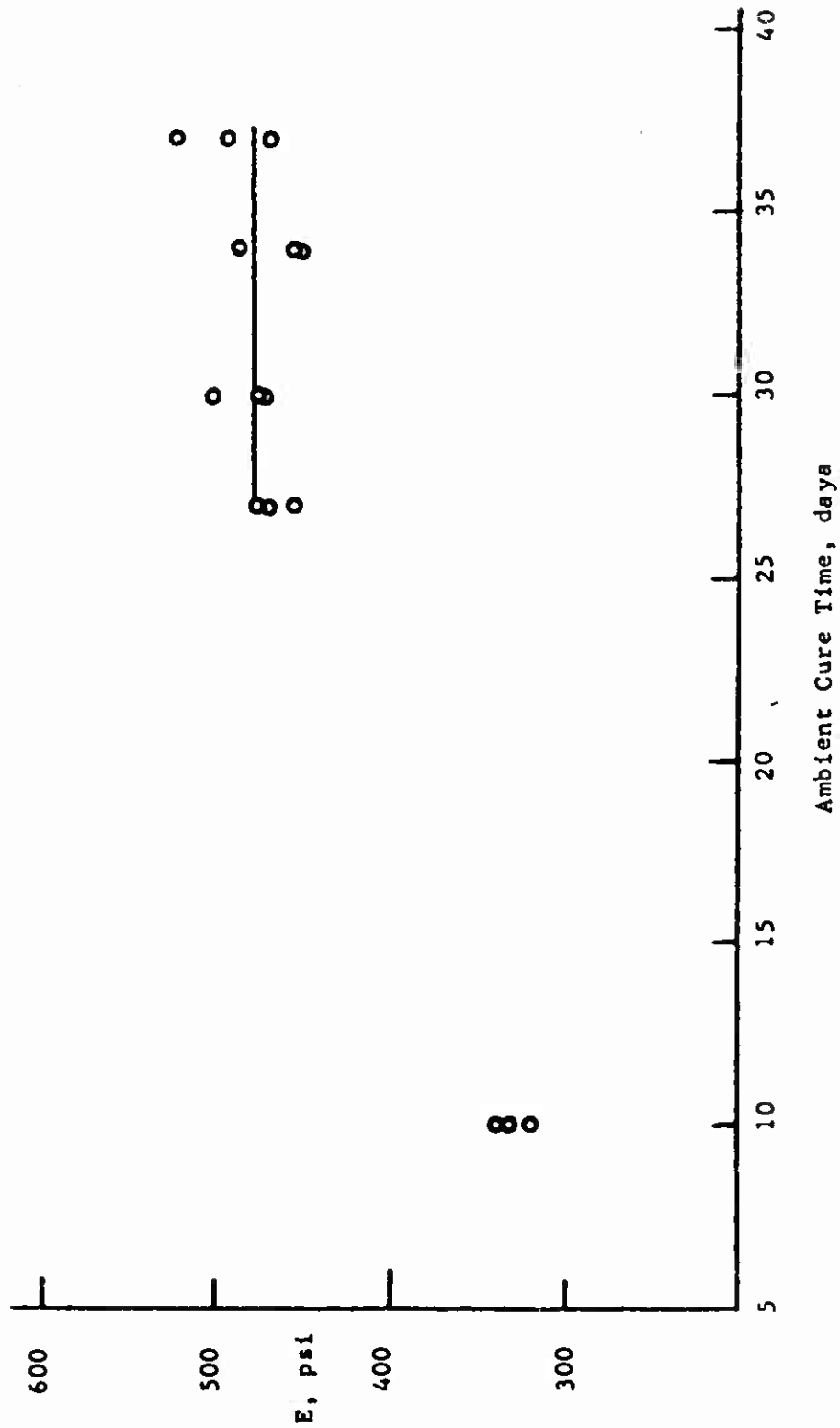
160

Figure 56 - Modulus vs. Cure Time for Propellant X237-78 (Telagen - HX-868, A/C = 0.70, CrOct = 1.0%)

Propellant X248-9, the 40-lb. casting of the baseline composition, had mechanical properties of 635/111/26 after 4 weeks cure at 75°F.

e. HC-434 - aziridine propellant: Since the Telagen-aziridine baseline propellant required twice the CrOct level as the epoxide-cured propellant, the first HC-434-aziridine propellant also used twice the epoxide cured baseline catalyst level, i.e., 0.9% CrOct in the binder (Table XL). Cure for this propellant, X237-64 (Figure 57), took about 4 weeks. Higher catalyst levels and lower A/C ratios were also tested since binder gumstock studies indicated these changes would bring about faster cure. A short pot life was obtained with 1.5 and 1.3% CrOct but the baseline propellant (X248-4) having 1.2% CrOct and an A/C of 0.75 had acceptable pot life. Cure for the baseline was nearly complete in 3 weeks although the propellant continued to harden slightly for 80 days, see Figure 58. No further work was scheduled or performed on HC-434-azirdine propellants.

f. PBAN - aziridine propellant: Of the six binder systems examined in propellants, the PBAN-aziridine was the most difficult to process and cure at ambient temperature. The catalyst requirements were very high compared to the PBAN/epoxide or the CTPB systems.

Binder System	Relative Concentration of CrOct Needed for Ambient Cure of Propellant
CTPB/Epoxide	1
CTPB/Aziridine	2-1/2
PBAN/Epoxide	4
PBAN/Aziridine	10

Another factor in processing was the higher viscosity of the PBAN prepolymer compared to the CTPB's.

A PBAN-aziridine propellant with an A/C = 1.0 and 5.0% CrOct in the binder phase was very viscous and slow to cure. Mechanical properties after 4 months at 75° ± 5°F were 760/60/15. A mix was prepared (X248-82) im which the A/C was lowered to 0.9 which, from the HC-434-aziridine binder study mentioned above should give a faster cure. Cure data are shown in Figure 59. Mix viscosity was 55 Kp and the cure time was greater than 9 weeks. A 10-lb. mix of this composition was made which was processable, (again lower viscosity was observed on scale-up) but cure time was greater than 5 months. No further work on this binder system was performed.

162

TABLE XL

HC-434 AZIRIDINE PROPELLANTS[a]

Notebook No.	CrOct	A/C	End of Mix Visc. at 26°C (Kp)	Visc. Kp/Time (Hr.)	Physical Properties at 77°F, 0.74 min^{-1}			Cure Time (days)
					Modulus (psi)	Strength (psi)	Strain at Max. Stress (%)	
X237-60	0.90	0.6	26	20/4	-	-	-	> 35
X237-64	0.90	0.8	27	21/4	550	134	34	35
X237-84	1.50	0.8	34	48/4	1,100	156	21	> 21
X248-81	1.30	0.7	30	43/4	630	134	29	28
X248-4	1.20	0.75	30	5/4	680	128	33	21

a/ Propellant composition is 32% 200 µ AP, 24% 130 µ AP, 24% 10-12 µ AP, 5% H-10 Al, 0.5% Fe$_2$O$_3$ and 14 .5% binder. The binder is 70% polymer and 30% IDP plasticizer and cure catalyst.
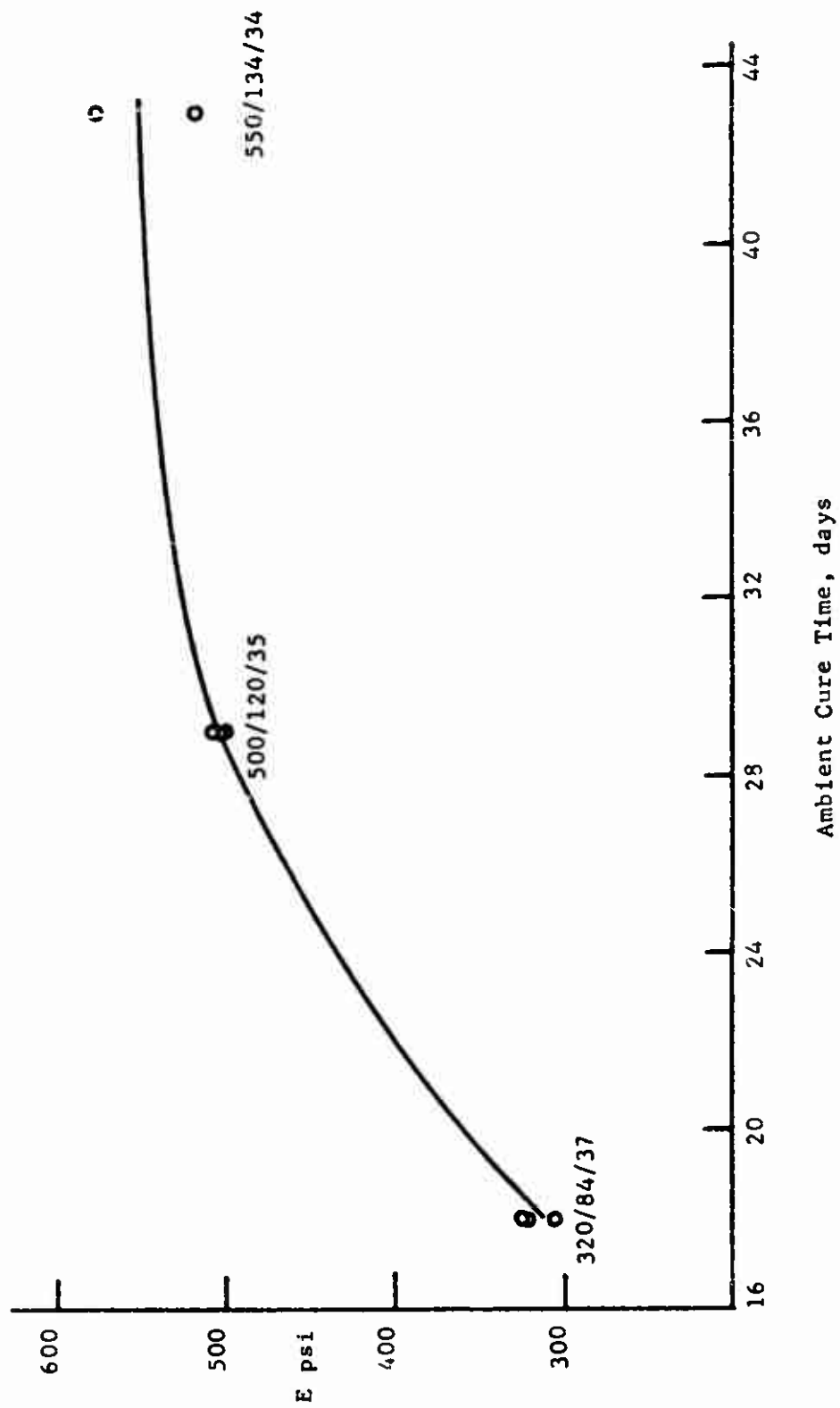
163

Figure 57 - Modulus vs. Cure Time for Propellant X237-64 (HC-434, Aziridine/Carboxyl = 0.80, CrOct = 0.90%)
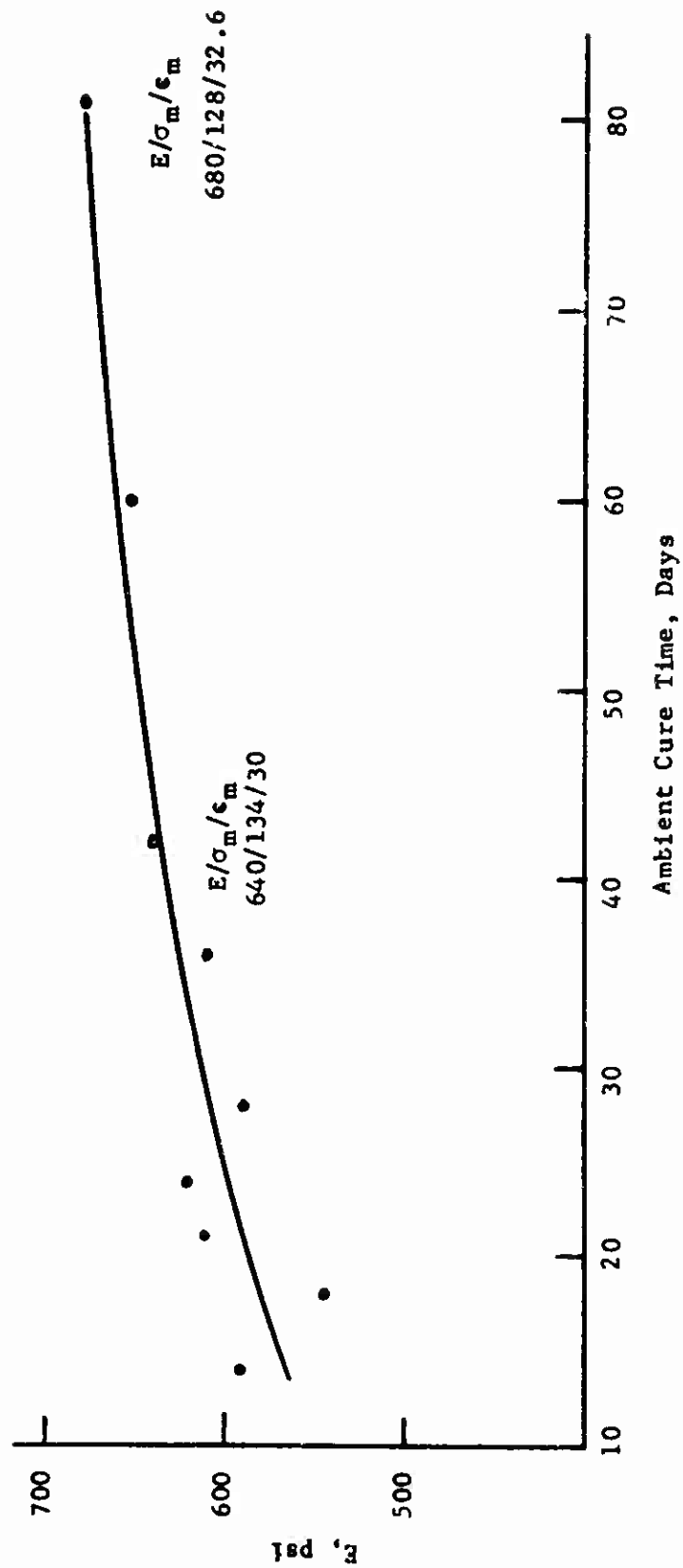
164

Figure 58 - Modulus vs. Cure Time for Propellant X248-4 (HC-434 - HX-868, A/C = 0.75, CrOct = 1.20%)
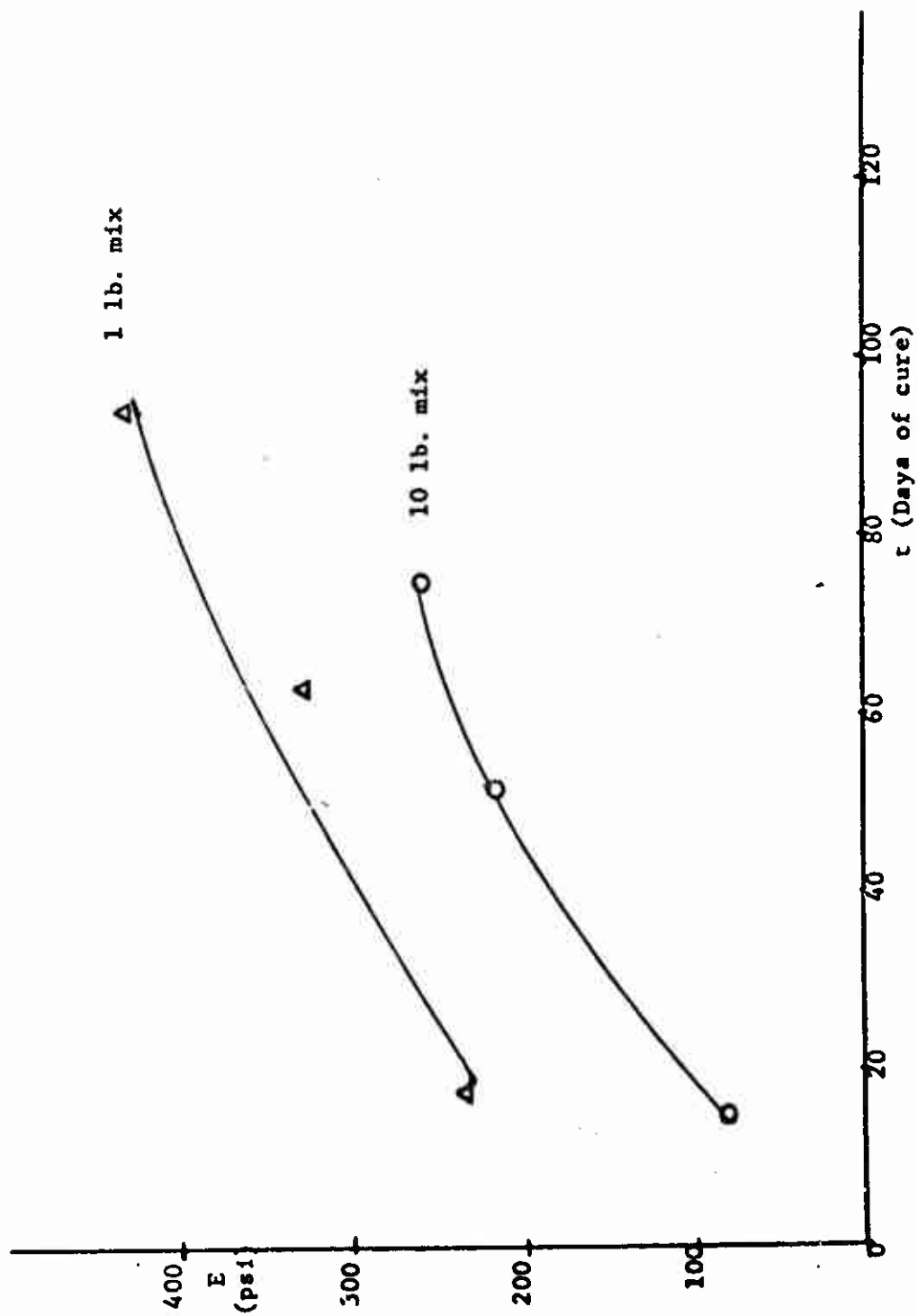
Figure 59 - PBAN-Aziridine Propellants

1 lb. mix

10 lb. mix

E
(psi)

400

300

200

100

20   40   60   80   100   120

t (Days of cure)

166

3. Effects of Other Constituents on Propellant Cure

a. _Other cure catalysts_: A 1-lb. Telagen epoxide baseline formulation was made with CrDIPS (chromium 2,6-diisopropyl salicylate) replacing CrOct on a chromium for chromium basis. After 18 days cure, the properties were only 76/25/50 while the CrOct baseline cures fully in about 10 days to properties of 390/113/43. After a 7-week cure at 75°F the CrDIPS propellant properties were 87/32/53. This propellant confirmed the binder gumstock studies conclusion that CrDIPS was inferior to CrOct as a carboxyl-epoxide cure catalyst.

b. _Water contaminant_: Water is the most likely contaminant to be present in composite propellants and its influence on catalyzed ambient cure was therefore given the most consideration of any of the contaminants tested.

Water was first tested as an added contaminant in the Telagen-epoxide baseline propellant. The quantity of water added was equal to the amount of CrOct present. The water was dissolved in THF and added to the propellant mix after all solids had been added. The mix viscosity was the same as for the baseline propellant 1-lb. mix. Cure was complete within 2 weeks at 75°F and final mechanical properties were 400/99/39. These properties compare well with those of the baseline except for an 11 psi drop in tensile strength. See Table XLI.

This propellant was then made on a 10-lb. scale (X237-66). Cure time was confirmed to be 2 weeks or less (Figure 60) and again a drop in tensile strength was observed (400/96/43) compared to the baseline propellant.

The Telagen-aziridine baseline was made with 0.5% water added to the binder. Cure time was unchanged but the final tensi'e strength was lowered (see Table XLI). Similar results were obtained when water was added to the PBAN-epoxide propellant.

It is therefore concluded that water contamination does not change the cure time but does lower ambient-cured propellant tensile strength. The other contaminants (Section C) were added as water solutions and the effects of the combined contaminants were expected to be additive.

c. _NH_3, $HClO_4$, HNO_3 and HF contaminants_: One-pound propellant mixes were prepared with the contaminants NH_3 and $HClO_4$ in the Telagen-epoxide baseline formulation. The contaminants were added as water solutions. The contaminant concentration was 0.01% of the propellant while the water concentration was at the same level (0.07%) as was tested

167

TABLE XLI

PROPELLANTS WITH CONTAMINANTS[a]

Contaminant/% of Binder	Baseline	Cure Time (Days)	Final Properties E (psi)	σ (psi)	ε_m (%)
None	Telagen-Epoxide	14	420	110	37
		17	390	116	44
H$_2$O/0.5		14	400	99	39
		21	400	96	43
NH$_3$		-	320	101	42
		21	370	83	40
HClO$_4$		21	310	78	33
		21	310	100	47
HNO$_3$		-	250	74	39
		28	260	80	43
HF		≤ 13	300	82	35
		8	350	99	40
None	Telagen-Aziridine	21	680	120	23
H$_2$O/0.5	Telagen-Aziridine	21	610	88	23
None	PBAN-Epoxide	28	500	95	31
H$_2$O/0.5	PBAN-Epoxide	≥ 28	500	80	24

a/ The first listing is the 1-lb. mix while the second set of values is from the 10-lb. castings.

168

Figure 60 - Modulus vs. Cure Time for Propellant X237-66 (Telagen-Epoxide, di/tri = 0.82, E/C = 0.75, CrOct = 0.75, 0.50%, H$_2$O = 0.50% of Binder)
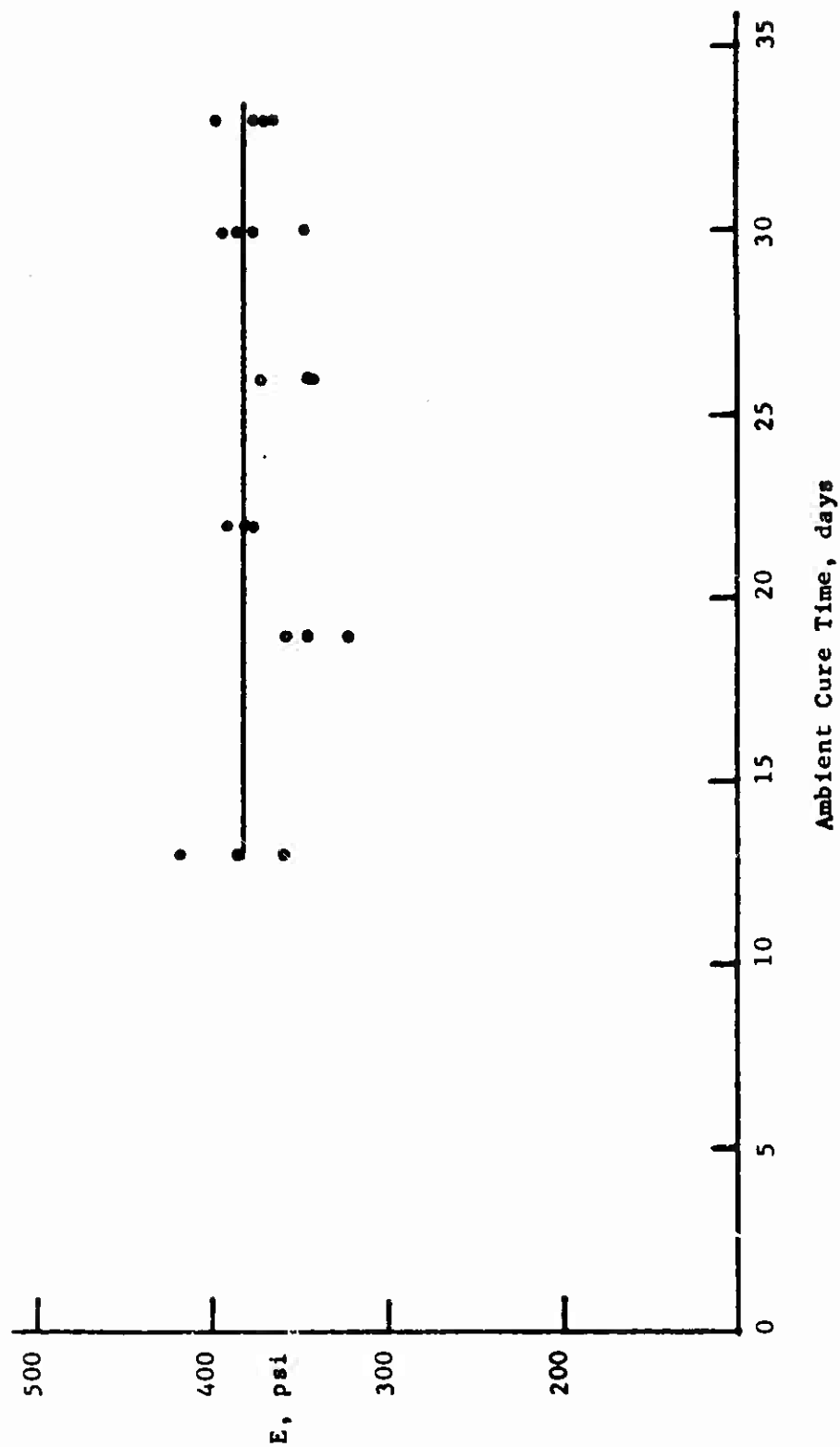
previsouly in the baseline propellant. Mix viscosities were normal, being 13 Kp at the end of mix. By periodically measuring mechanical properties of these two propellants, it was determined that cure time ($\approx$ 2 weeks) at $75 \pm 5°F$ was unaffected by the contaminants but that final properties, particularly in the case of $HClO_4$, may have been affected. Final properties of the 1-lb. control propellant were (E, psi/σ_m, psi/ϵ_m, %) 400/99/39 while those of the NH_3 and $HClO_4$ propellants were 320/101/42 and 310/78/33, respectively. The lower tensile strength of the $HClO_4$-containing propellant is particularly at variance with the control propellant.

Propellants were made in the same fashion with HNO_3 and HF contaminants. Mechanical properties after 24 days of ambient cure were 250/74/39 and 300/82/35, respectively. All four propellants had lower moduli than the control which probably indicate some loss of epoxide curative, perhaps due to homopolymerization catalyzed by the presence of acid.

Cure studies were then performed on a 10-lb. scale with each of the four contaminants in the Telagen-epoxide baseline formulation. Cure time and final properties are given in Table XLI. The only feature which stands out is the short cure time in the HF-contaminated propellant. This was in contrast to the model system experiments performed at MRI which indicated that HF only consumed epoxide.

d. Oxamide: One of the ingredients to be tested for its effect on ambient-cured propellants was oxamide. A propellant (X237-69) was prepared of the Telagen-epoxide baseline composition in which 4% of the fine AP was replaced with oxamide. The propellant cured normally; however, the mix unexpectedly had a short pot life. Two additional 1-lb. propellant mixes were made, which used a new lot (ABL No. 4) of oxamide. The pot life results are shown in Table XLII. Evidently oxamide does shorten the pot life of these ambient cured propellants with the "lab sample" being particularly active.

e. Thiodiphenylamine: Another additive to be tested was the antioxidant thiodiphenylamine (TDPA). This was added to Telagen propellant of the type X222-16 at a 1% level in the binder. The TDPA propellant (X222-34, Table XXXVII) cured more slowly and was weaker than the control as can be seen in Figure 61. Since this behavior could be due to a loss in epoxide, because of a reaction between TDPA and the epoxides, another composition (X222-85) was prepared in which the amount of triepoxide (ERLA-0510) was increased by a quantity equivalent to the TDPA added. This propellant cured at a good rate (see Figure 61) and was stronger. From this result it was concluded that, in the propellant environment, TDPA probably reacts with the epoxides but that the equivalent weight

TABLE XLII

EFFECT OF OXAMIDE ON SLURRY
VISCOSITY OF TELAGEN-EPOXIDE PROPELLANT

Mix Number	Oxamide Lot Number	(%)	Viscosity[a] (Kp)
X-237-25	-	0	13
X-237-69	Lab Sample	4.0	42
X-248-98	ABL No. 4	4.0	32
X-248-44	ABL No. 4	4.0	28

a/ Measured at 77°F, 4 hr. after cure catalyst addition.
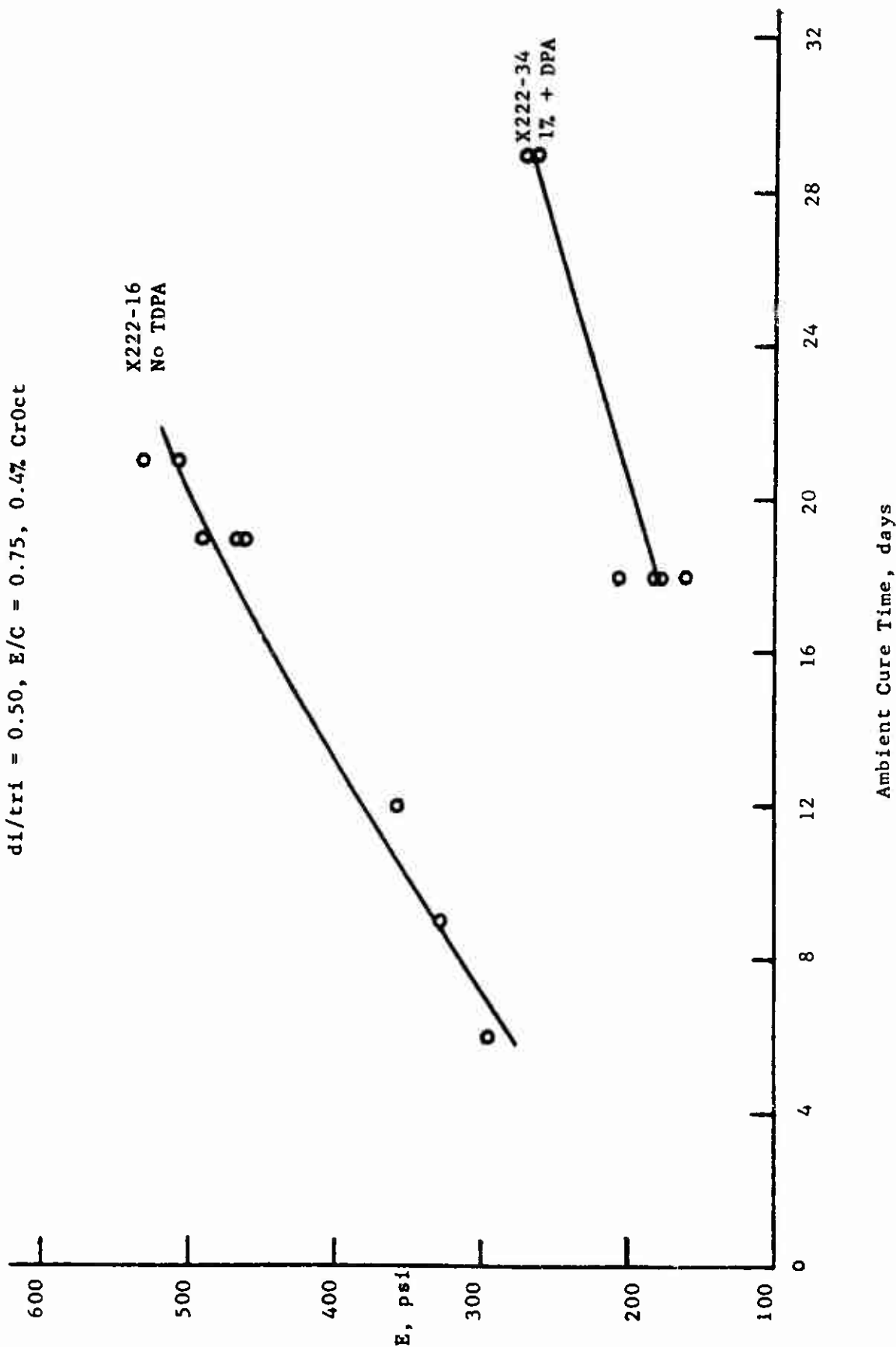
dl/tri = 0.50, E/C = 0.75, 0.4% CrOct

X222-16
No TDPA

X222-34
1% + DPA

Figure 61 - Modulus vs. Cure Time for Telagen Propellants
(dl/tri = 0.50, E/C = 0.75, 0.4% CrOct)

Ambient Cure Time, days

E, psi

172

of the TDPA is higher than the theoretical value. Loss of cure catalyst may also explain the observed behavior.

TDPA was again tested in the Telagen-epoxide baseline propellant. As in the previous Telagen case, 1% TDPA was added to the binder. This propellant (X237-54) cured on the normal time schedule but was softer than the baseline propellant. Confirming the previous finding that loss of curatives, when TDPA is present, is significant in ambient-cured propellants. This does not happen at 140°F cure temperature.

f. CrOct as a slurry viscosity depressant: It was reported above that CrOct was a surfactant in the CTPB system. This was verified by comparing the viscosities of Telagen-epoxide baseline formulations with and without CrOct at 75°F. The slurry made with 0.0725% CrOct had a viscosity of 16 Kp while the identical slurry made without CrOct had a viscosity of 50-80 Kp. A more exact determination of viscosity could not be made because, above 50 Kp, the slurry had a tendency to rotate with the bob instead of being sheared between cup and bob in the Rotovisco.

g. Mix cycle variation: In our normal mix cycle chromium octoate was added last. Since chromium octoate is a surfactant for these propellants, it was thought that processing might be improved if the cure catalyst could be added to the mix earlier. In Telagen-epoxide propellant X237-48 CrOct was present in the binder premix and the two epoxides were added last. The mix was, as expected, of lower viscosity when the epoxides were added last relative to the mix viscosity when CrOct was added last. After addition of the epoxides the viscosity visibly increased so that the end of mix viscosity was about normal for the 1-lb. baseline propellant. The propellant cured in the normal time period but the strength was quite low (220/66/42).

A repeat of propellant X237-48 was made in which CrOct was in the binder premix and a mixture of the two epoxides was added last. The repeat mix, X248-2, duplicated the properties of the original mix in every respect.

We have observed that ambient-cured propellants and unfilled binders of identical stoichiometries can vary in strength, when cured, if the quantity of cure catalyst is varied. Propellants and binders with lower catalyst levels have lower strength. A possible explanation for obtaining softer propellant when the CrOct was added to the premix was that some of the CrOct prereacted somehow and the effective catalyst concentration was lowered. The cause for this apparent loss in CrOct to the system is not understood. Under this reverse addition, the CrOct has an opportunity to more completely react with the carboxyls on the CTPB

173

before the epoxide was introduced, but this was not expected to effectively remove catalyst from the system.

4. Surveillance:

a. Results: Under Phase IV, Large-Scale Demonstration, the effects of catalyzed ambient temperature cure on the storage life of propellant was to be measured and compared to the storage life of 140°F-cured propellant. Ten propellant compositions were selected for the surveillance phase. These consisted of four 75°F-cured baseline propellants, two 75°F-cured baseline propellants with water contaminant added and four 140°F-cured control propellants. These propellants are listed in Table XLIII along with their initial mechanical properties. A 40-lb. batch of each propellant was made, then cut into ten 2 in. x 4 in. x 6 in. blocks and placed in controlled storage. The surveillance schedule was:

Temperature	Time - Months					
	1	2	3	4	5	6
75 ± 5°F			X			X
160 ± 5°F		X		X		X

Some 12-month surveillance measurements were also made. Mechanical properties were measured on propellant in the interior ($\sim$ 1/2-in. from any surface) of each block at the specified time intervals. By testing interior propellant, mechanical property changes due to air oxidation were minimized.

The gel content of the propellant at the surface of these aged blocks was determined and compared with the gel content of the interior propellant to separate the effects of oxidative crosslinking from bulk propellant reactions. Two temperatures were chosen for the surveillance: vis., the 75°F cure temperature and an accelerated aging temperature of 160°F.

Mechanical property and gel content results of the 6-months surveillance are shown in Tables XLIV and XLV. Twelve-month aging data are given in Table XLVI. Figures 62 and 63 show the change in modulus with time and temperature for the Telagen baseline and heated-cured control propellants.

For the Telagen-epoxide propellants, the ambient-cured grain aged in a fashion similar to the 140°F-cured grain and the ambient baseline with water added aged as well as the baseline. There was only a small drop in modulus and tensile strength during ambient aging in each and had a larger loss due to 160°F aging. Gel content was nearly constant in each case.

TABLE XLIII

PROPELLANTS FOR SURVEILLANCE[a]

Type	Batch Number	Crosslinker/ Carboxyl	di/tri Crosslinker Functionality	% CrOct in Binder	Cure Time[c] (Days) at 75°F	Cure Time[c] (Days) at 140°F	Modulus (psi)[d]	Tensile Strength (psi)[d]	Strain at Max. Stress (%)[d]
Telagen-Epoxide Baseline	X237-71	0.75	0.82	0.50	14	-	390	113	43
Telagen-Epoxide with water[b]	X248-15	0.75	0.82	0.50	14	-	380	97	41
Telagen-Epoxide heated cure	X237-72	0.92	0.82	0.12	-	7	480	120	38
Telagen-Aziridine Baseline	X248-9	0.70	tri	1.00	21	-	635	111	26
Telagen-Aziridine with water[b]	X248-22	0.70	tri	1.00	21	-	500	101	33
Telagen-Aziridine heated cure	X248-35	1.00	tri	0.40	-	7	470	130	45
HC-434-Epoxide Baseline	X237-81	0.75	0.50	0.45	14	-	690	146	41
HC-434-Epoxide heated cure	X248-23	0.87	0.50	0.12	-	7	1,060	140	23
PBAN-Epoxide Baseline	X248-21	1.00	tri	1.75	26	-	400	78	31
PBAN-Epoxide heated cure	X248-37	1.00	tri	0.40	-	7	695	96	22

a/ Propellant composition - 32% 200 μ AP, 24% 130 μ AP, 24% 10-13 μ AP, 5% H-10A1, 0.5% Fe_2O_3 and 14.5% binder. The binder is 70% polymer and 30% IDP plasticizer and cure catalyst.

b/ Amount of water added is equal to amount of CrOct present.

c/ Cure time at 75°F was determined by testing 10-lb. mixes.

d/ Mechanical properties were measured and surveillance begun 7 days after 75°F cure time to assure complete cure.

175

TABLE XLIV

SURVEILLANCE OF 40 POUND BATCHES_a/ TELAGEN PROPELLANTS

Mechanical Properties
Modulus (psi)/Tensile Strength (psi)/Strain at Maximum Stress (%)
77°F, 0.74 in/in/min at Various Aging Time and Temperatures

Propellant	Initial	Aging at 75°F		Aging at 160°F		
		3 Months	6 Months	2 Months	4 Months	6 Months
1. Ambient-Cured Telagen-Epoxide	420/112/41	430/115/41	400/108/42	330/91/43	300/79/44	219/59/42
2. 140°F-Cured Telagen-Epoxide	480/120/38	480/110/35	449/99/34	410/105/39	340/105/49	285/98/54
3. Ambient-Cured Telagen-Epoxide with H₂0 added	380/97/41	365/103/44	353/108/45	290/82/42	236/71/45	223/63/44
4. Ambient-Cured Telagen-Aziridine	635/111/26	813/140/25	763/144/26	590/137/32	534/115/31	490/103/29
5. 140°F-Cured Telagen-Aziridine	470/130/45	577/140/36	530/145/43	390/117/45	260/86/51	263/81/50
6. Ambient-Cured Telagen-Aziridine with H₂0 added	500/101/33	522/113/34	512/111/35	380/89/34	293/65/37	213/52/39
HC-434 Propellants						
7. Ambient-Cured HC-434-Epoxide	690/146/41	760/143/36	461/117/48	650/122/36	440/119/48	332/103/58
8. 140°F-Cured HC-434-Epoxide	1060/140/23	998/129/21	870/131/25	770/130/30	650/130/35	540/138/43
PBAN Propellants						
9. Ambient-Cured PBAN-Epoxide	400/78/31	613/73/17	689/81/17	820/93/17	872/95/16	898/101/17
10. 140°F-Cured PBAN-Epoxide	695/96/22	869/109/18	945/117/20	835/109/19.4	946/116/19	980/121/19

a/ Cut into 2 in. x 4 in. x 6 in. blocks and wrapped in aluminum foil.

TABLE XLV

BINDER GEL CONTENT AND MODULUS OF SURVEILLANCE PROPELLANTS

Propellant			Gel Content of Binder				Propellant Modulus	
			6 Month Ambient	2 Months 160°F	4 Months 160°F	6 Months 160°F	6 Months Ambient (psi)	6 Months 160°F (psi)
1.	Ambient-Cured	Interior[a]	37.2 (38.3)	-	40.2	34.4	400	219
	Telagen-Epoxide	Surface[b]	36.9 (38.1)	-	43.7	44.6	-	-
2.	140°F Cured	Interior	50.3 (51.1)	-	50.4	47.5	449	285
	Telagen-Epoxide	Surface	50.3 (51.0)	-	53.2	51.2	-	-
3.	Ambient-Cured	Interior	- (39.5)	42.8	54.3	41.0	353	223
	Telagen-Epoxide with H_2O added	Surface	- (41.7)	43.0	41.0	49.9	-	-
4.	Ambient-Cured	Interior	45.3 (45.2)	44.1	39.2	41.8	763	490
	Telagen-Aziridine	Surface	44.5 (45.7)	45.0	44.2	49.3	-	-
5.	140°F-Cured	Interior	(45.7)		38.8	41.2	530	263
	Telagen-Aziridine	Surface	(43.4)		48.9	47.6	-	-
6.	Ambient-Cured	Interior	- (41.3)	38.0	31.7	24.1	512	213
	Telagen-Aziridine with H_2O added	Surface	- (39.2)	46.1	49.5	47.6	-	-
7.	Ambient-Cured	Interior	38.7 (41.0)	-	42.2	38.1	461	332
	HC-434-Epoxide	Surface	39.2 (41.5)	-	33.?	30.6	-	-
8.	140°F-Cured	Interior	67.6	-	57.0	59.9	870	540
	HC-434-Epoxide	Surface	67.2	-	54.9	53.7	-	-
9.	Ambient-Cured	Interior	- (35.9)	40.6	39.4	38.4	689	898
	PBAN-Epoxide	Surface	- (36.5)	38.4	37.5	37.2	-	-
10.	140°F-Cured	Interior	- (34.9)	-	34.9	35.4	945	980
	PBAN-Epoxide	Surface	(34.6)	-	34.8	34.3	-	-

a/ Gel content of propellant (expressed as percent of binder) from the interior of the block.
b/ Gel content of propellant from the surface of the block
Note: ( ) "3" month at ambient samples that were tested for gel content after 6 months at ambient.

TABLE XLVI

TWELVE-MONTH AGING PROPELLANT PROPERTIES

Propellant	Mechanical Properties at 77°F, 0.74 in/in/min		
	Modulus (psi)	Strength (psi)	Strain at Max. Stress (%)
Ambient-Cured Telagen-Epoxide			
Aged 75°F	430	112	39
Aged 160°F	260	63	38
140°F-Cured Telagen-Epoxide			
Aged 75°F	470	112	37
Aged 160°F	290	100	51
Ambient-Cured HC-434-Epoxide			
Aged 75°F	430	112	45
Aged 160°F	330	92	49
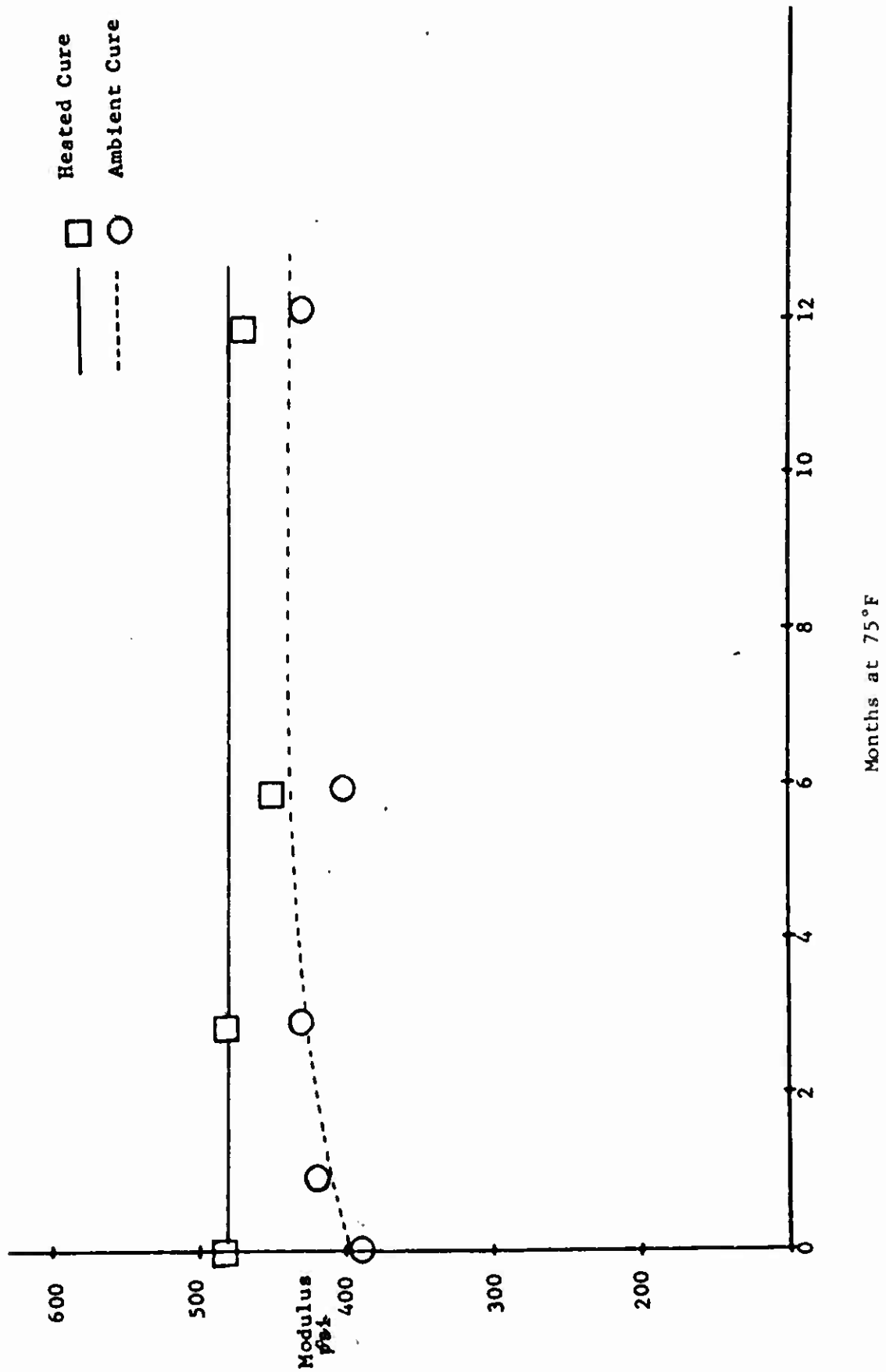
Figure 62 - Telagen Epoxide Propellants Aged at Ambient

Months at 75°F

Heated Cure

Ambient Cure

Modulus
psi

600
500
400
300
200
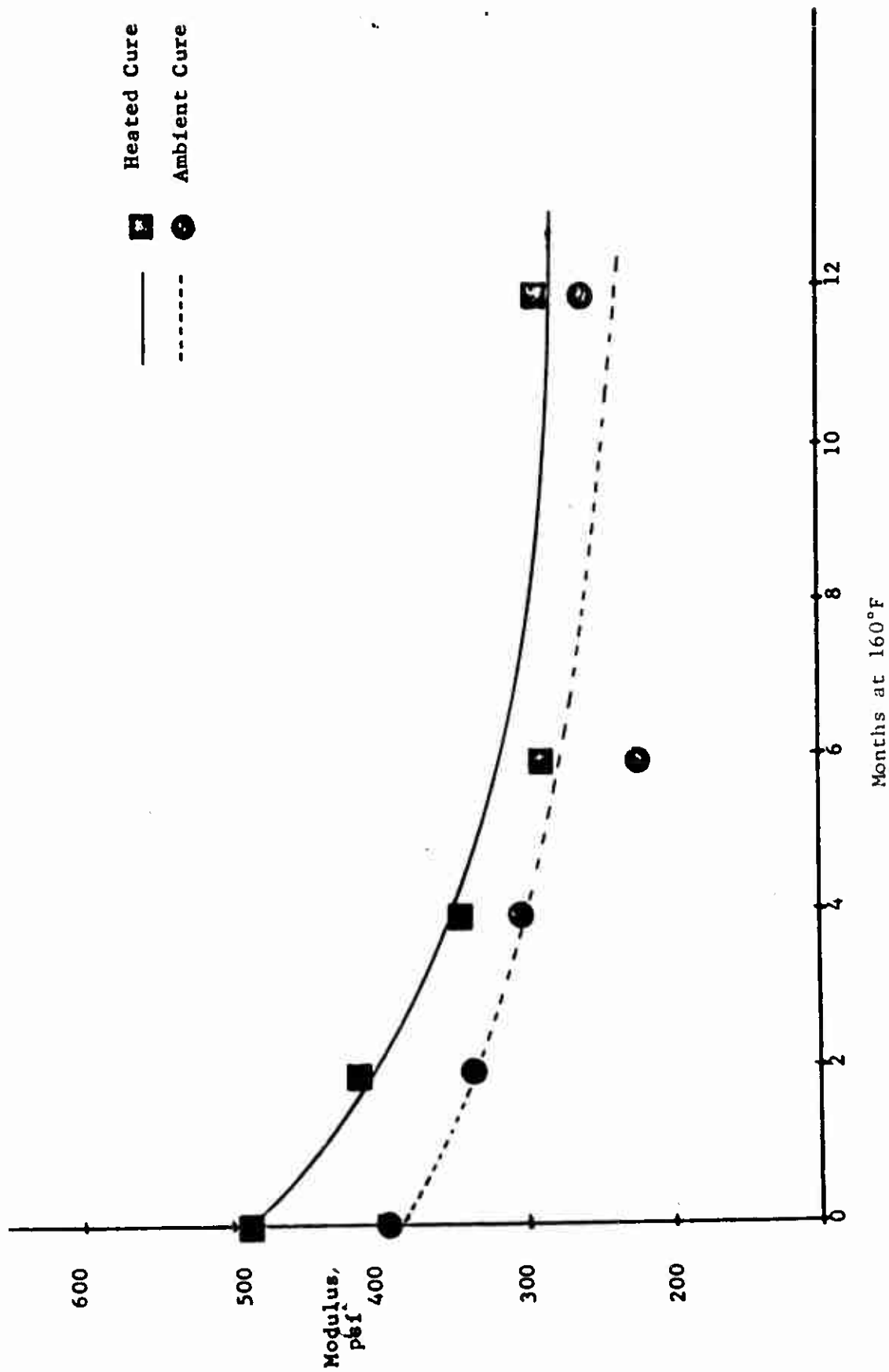
2   4   6   8   10   12

Figure 63 - Telagen Epoxide Propellants Aged at 160°F

Ambient cure with high CrOct level did not materially affect the aging characteristics of Telagen-epoxide propellant.

The three Telagen-aziridine propellants had small increasea in modulus and tensile strength on ambient aging which ahows that post-cure of the ambient cured propellants was the aame as for the 140°F-cured propellant. When aged at 160°F the propellants eventually lost strength. In this case, the heated control and water-contaminated baseline had high losses in strength while the baseline did not. The two HC-434-epoxide propellants lost modulus and tensile strength on aging, hoth at 75° and 160°F. The modulus losses were similar.

The two PBAN-epoxide propellants post-cured both at ambient and 160°F to about equal degrees. Therefore, ambient-cured propellants age as well as the 140°F-cured control propellants. There was no evidence that the higher degree of deaired cure reaction, described below, improved the aging characteristics of ambient-cured propellants. It had been speculated that a higher degree of stable ester crosslinks in the binder of the ambient-cured propellants would provide better aging stability relative to the 140°F-cured propellants.

It was expected that, with aging, the exterior of a propellant block would increase in gel content relative to the interior due to air-induced oxidative crosslinking of the surface. All of the 6-month-at-160°F propellants, except the HC-434, had higher gel content at the surface than in the interior of the blocks. Both the ambient and 140°F-cured HC-434 propellants exhibited anomalously low gel contents at the surface after 6 months at 160°F.

One general conclusion that can be drawn is that there appears to be a general oxidative crosslinking effect on the surface of 160°F-aged specimens made with Telagen.

It should be noted that this measure of gel in the system is only a gross measure of the crosslinks, not to be confused with the effective crosslink density defined by the Flory - Rehner (Ref. 9) or Mooney (Ref. 10) - Rivlin (Ref. 4) equations.

b. The ambient cure reaction: It was discovered that catalyzed ambient cure of these propellants required less crosslinking agent than did 140°F cure in order to obtain equivalent mechanical properties. This demonstrates that cure at ambient means that a higher degree of the desired crosslinking reaction is occurring than in 140°F cure, where loss of curative takes place due to side reactions.

This was noticed when the 140°F-cured control propellants for the surveillance program were being made. A Telagen-epoxide 1-lb. mix was made of the baseline formulation in which the only change was to reduce the CrOct concentration from 0.50 to 0.12% of the binder. Good pot life was obtained and cure was complete in 7 days but mechanical properties (modulus 130 psi, tensile strength 56 psi, strain at maximum stress 62%) indicated a very low gel content. Some loss in strength was expected, compared to the ambient-cured propellants, since undesired side reactions take place to a higher degree at 140°F. However, the magnitude of this loss in strength was not expected. It was necessary to increase the E/C from 0.75 to 0.92 to give a 140°F-cured propellant with good mechanical properties. Similar occurrences took place in the Telagen-aziridine and HC-434 epoxide cases (see Table XLIII).

However, there is still a loss of curative to side reactions taking place during ambient cure. This is evidenced by the fact that propellants with high CrOct levels have not only a shorter cure time but also yield stronger propellant; for example, propellants X196-87 and X222-12 in Table XXXVI, X222-61 and X222-95 or X237-21 and 27 in Table XXXVII. This indicates that when cure is slower and there is more time for side reactions to occur, that they will occur even at ambient.

XI.

EXPERIMENTAL

A. Model System Studies

1. Experimental considerations: The analytical requirements for the kinetic study system were as follows:

a. The rate of the reaction must be followed quantitatively and accurately.

b. The stcchiometry of the reaction must be followed, that is, the rates of disappearance of reactants should be followed simultaneously.

c. The rate of product formation should be readily determinable. This applies to the expected product plus any side products formed.

d. A means of indicating the products, especially side products should be available.

e. The entire technique should be as rapid and inexpensive as possible.

f. It would be desirable if all these requirements could be met in as few manipulations as possible.

The use of gas liquid chromatography comes close to meeting all the requirements enumerated above. Aliquots are withdrawn from the reaction vessel periodically and analyzed by GLC. The chromatograph indicates the total number of components present in the sample at that time. From retention time these components can be identified and relative concentration of components calculated.

2. Experimental procedures:

a. The internal standardization method was used to calibrate the gas chromatography method for quantitative analysis of the reaction mixtures. Known weight or mole ratios of the sample and a standard were prepared and chromatographed. The peak areas are measured. Area ratios

are plotted against weight or mole ratios to obtain a calibration curve. An accurately known amount of the internal standard is then added to the unknown sample and the mixture chromatographed. Area ratios are measured and from the calibration graph the weight ratio of the unknown to the standard is known.

The advantages of this calibration method are that the quantitites injected need not be measured accurately and the detector response need not be known or remain constant since any change in response will not alter the area ratio.

An internal standard must:

1. Be well resolved from the other peaks;

2. Be eluted close to the peaks of interest;

3. Be approximately the same concentration as the unknown; and

4. Have a structural similarity to the unknown.

Peak height measurement is more rapid than peak area; however, plots of peak height vs. sample size have a more limited linear range than corresponding plots for peak area. Peak height and width are frequently dependent on sample size and sample feed volume while peak area is not.

After optimization of gas chromatographic conditions to give good separations (i.e., convenient retention and sharp peaks reproducibly), calibration curves were prepared using toluene as solvent and internal standard for AGE, epoxy butane, EHA, and octanoic acid and for the AGE-EHA combination. After establishment of the calibration plot its reproducibility was demonstrated on several test solutions. Variation in sample size between 1 and 2 µl. was shown not to affect the reproducibility of the peak height integration method.

b. Summary of GC conditions:

Column packing	20% SF-96 on Chromosorb P (60/80 mesh), silanized
Column dimensions	6 ft. x 1/4 in. aluminum
Temperature	100° to 275°C
Heating rate	10°C/min

184

Gas flow rate	80 cc/min (helium)
Block temperature	275°C
Bridge current	175 ma.
Injection temperature	275°C

c. Catalyst screening runs: Stock solutions containing equimolar quantities of reactants are prepared in advance of a given series. A typical composition is given below:

Component	Moles	Weight	Weight (%)
Allyl glycidyl ether	0.204	23.256	22.342
2-Ethyl hexanoic acid	0.203	29.232	28.083
Toluene		51.600	49.573

Five milliliters of this solution are added to a vial, 1% by weight catalyst is added (0.0447 g.); the vial is sealed with a serum cap and subjected to the desired environmental conditions. At prescribed time intervals samples are removed by hypodermic syringe and subjected to GC analysis. Solution loss does not occur using this method.

B. Infrared Analysis of Cure Systems

Absorbance changes in the infrared spectrum of binder mixtures provides a method for observing reaction rates in neat cure systems (Refs. 4 and 5).

Cure reaction formulations are prepared in small sample vials. A sample of known weight is transferred to a salt disc fitted with a Teflon spacer. A second salt disc is placed over the sample and spacer to complete the test specimen. The resulting cell is gently compressed in a nut and screw type ball joint clamp to expel air and to evenly distribute the cure formulation in the cavity between the salt discs. At temperatures as high as 100°C, the use of NaCl plates was shown not to have a catalytic effect on the reaction (Refs. 4 and 6).

The absorbance changes are noted at carbonyl bands related to COOH at 5.9 μ and to COOR at 5.8 μ. In the Telagen CT systems characteristic absorbance bands of the ethylenic group at 5.5 μ and 6.1 μ serve as convenient internal standard points for quantitative observations of the acid-to-ester conversion which takes place during the cure.

185

A secondary group of bands, one at 2.9 μ related to development of CHOH and one at 3.2 μ due to COOH are also employed for noting changes during the progress of cures. The baseline absorbances at 2.7 μ and 4.7 μ are convenient reference points for quantitative estimation of changes in the two components as they occur.

Cell thicknesses for conducting the analyses were established to be 0.050 mm. for observing changes in the 5.8-μ and 5.9-μ bands and 0.20 mm. for noting changes in the 2.9-μ and 3.2-μ bands.

The baseline method was used to measure absorbances. A calibration curve relating absorbance ratios (5.8 and 5.9 to 6.1 μ) to concentration (meq) of carboxylic acid and ester was established as follows: A series of CTPB samples containing different ratios of ester to acid were prepared by esterification of CTPB with less than equivalent amounts of epoxybutane. Residual acid content in each sample was determined by titration. The calibration curve was then established by relating the known acid and ester concentrations of the various samples to their respective infrared responses.

As the cure reaction proceeds, the intensity of the COOH peak at 5.9 μ decreases continuously while the ester peaks at 5.8 μg. During the latter stages of the conversion, the 5.9 μ peak is visible only as a shoulder in the spectrum and carboxylic acid content cannot be determined accurately by IR at this point. In this region, the extent of reaction was determined from the ester peak intensity-concentration relationship.

C. Gumstock Studies

The method employed was to prepare 30-g. mixes of the binder consisting of 70% polymer, the specified quantity of cure catalyst and solids, and the remainder DOA. The binder was evacuated and cast into four 8-in. long by 1/4-in. diameter Teflon tubes. After cure for the specified time period, the binder was removed from the Teflon tube and specimens were prepared. Duplicate mechanical property specimens (1/4-in. by 1-in. cylinders) were prepared by epoxy bonding to wooden end tabs. The samples were pulled on an Instron tester at a strain rate of 1 in/in/min until 35% elongation. The secant modulus at 30% elongation was then calculated. Samples were not tested until break because with an E/C of 1 and the use of all tri-epoxide, frequently, the binder is stronger than the bond to the wooden end tab which results in specimens breaking at the bond rather than within the binder phase. The bond was always strong enough to take the specimen to 30% elongation.

Gel content was determined on a 1-g. binder sample by a 48-hr. methylene chloride extraction which was followed by a 4-day acetone extraction when AP was present. Gel samples had a 1/16-in. web thickness. Linear swelling was determined on duplicate 1-in. long specimens in contact with benzene for 3 days. The benzene was replaced with fresh solvent on each of the first 2 days.

D. Propellant Mixes

The 1-lb. propellant mixes were manufactured in a 1-qt. Baker-Perkins double vertical planetary mixer. The solids were added incrementally and the CrOct was added as a THF solution 40 min. before the end of the mix cycle. Viscosities were measured on a Haake rotoviscometer at 26°C, and the values at a shear rate of 0.411 sec^{-1} are reported in Table XVII. Propellant mechanical properties were measured on Type II JANAF tensile specimens using the Instron tester and a strain rate of 0.74 in/in/min.

E. Materials

The acids, 2-ethyl hexanoic, octanoic, and propionic, and the epoxides-- epoxy butane and allyl glycidyl ether--were all reagent grade and supplied by Matheson Chemical Company. The polymer cure studies employed liquid carboxyl-terminated polybutadiene (CTPS) with an equivalent weight of 2,990 supplied by General Tire and Rubber Company and the epoxides ERLA-0510 (97-101 equivalent weight) supplied by Union Carbide and DER-332 (1.2-174 equivalent weight) from Dow. Moat of the metal salts used in the screening studies were obtained from Shepherd Chemical Company.

XII.

CONCLUSIONS AND RECOMMENDATIONS

1. Propellants based on carboxylic acid-epoxide and carboxylic acid-aziridine binder systems and containing up to 85.5% solids (AP, Al) can be mixed, cast, and cured completely and successfully at 25° ± 1°C. High solids loadings and ease of processing are possible because the chromium catalyst used (Cr 2-ethyl hexanoate) acts as a surfactant at the concentration level employed. The binder prepolymers to which this cure system has been applied include Telagen CT, PBAN, and HC-434.

2. For the ambient cure system, chromium salts are excellent catalysts for both epoxide and aziridine systems. Catalyst levels vary from 0.5 to 1.5 wt. % of the binder depending on the specific prepolymer.

3. Certain propellant ingredients and additives were shown to affect processing and/or cure. Minor adjustments in the formulation will compensate for the observed effects.

4. Surveillance studies of model, binder, and propel.ant samples have shown no detrimental aging effects due to the presence of the cure catalyst. The CrOct catalyzed propellants age as well as 140°F cured control propellants.

5. The Telagen-epoxide ambient-cured binder system is ready for scale-up beyond the 40-lb. batch scale size, 85.5% total solids propellant demonstrated in this program.

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GLOSSARY OF TERMS

Oct   Octoate - commercial; 2-ethyl hexanoate

neo-dec   neo-decanoate $CH_3(CH_2)_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}H-CO_2^-$

AO-2246   [2,2-Methylene-bis-(methyl-6-tert-butyl)phenol]
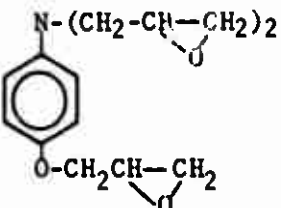
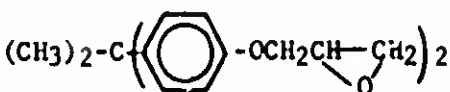Phenyl-β-N   Phenyl-β-naphthylamine

Roccal   Alkyl phenylenediamine

AGE   Allyl glycidyl ether $CH_2\overset{\overset{\displaystyle O}{\diagup\diagdown}}{-}CH-CH_2OCH_2CH=CH_2$

EHA   2-Ethyl hexanoic acid

OA   Octanoic acid

EB   Epoxybutane

ERLA 0510

DER 332 $(CH_3)_2-C{\Large(}⬡{\Large)}_2-OCH_2CH\overset{\overset{\displaystyle }{}}{-}CH_2\Big)_2$

AA   Acetylacetonate

TDPA   Thiodiphenylamine

AcAz

R $\quad$ R

R $= -\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{N}\underset{\text{CH-CH}_3}{\overset{\text{CH-CH}_3}{<}}$ $\underline{cis}$

BITA (HX-868)

R $\quad$ R

R $= -\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{N}\underset{\text{CH}_2}{\overset{\text{CH-C}_2\text{H}_5}{<}}$

MAPO

$\overset{\text{O}}{\underset{}{\|}}\text{P}\left(-\text{N}\underset{\text{CH}_2}{\overset{\text{CH}_3}{<}}\right)_3$

MAPS

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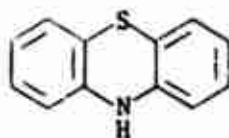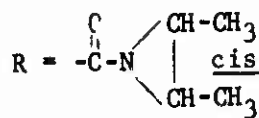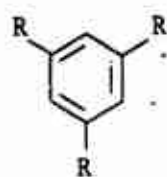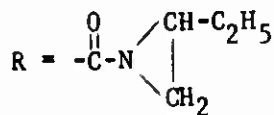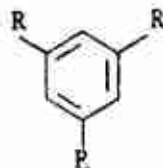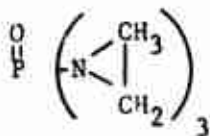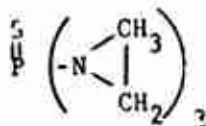
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13. ABSTRACT

1. Propellants based on carboxylic acid-epoxide and carboxylic acid-aziridine binder systems and containing up to 85.5% solids (AP, Al) can be mixed, cast, and cured completely and successfully at $25° \pm 1°C$. High solids loadings and ease of processing are possible because the chromium catalyst used (Cr 2-ethyl hexanoate) acts as a surfactant at the concentration level employed. The binder prepolymers to which this cure system has been applied include Telagen CT, PBAN, and HC-434.

2. For the ambient cure system, chromium salts are excellent catalysts for both epoxide and aziridine systems. Catalyst levels vary from 0.5 to 1.5 wt. % of the binder depending on the specific prepolymer.

3. Certain propellant ingredients and additives were shown to affect processing and/or cure. Minor adjustments in the formulation will compensate for the observed effects.

4. Surveillance studies of model, binder, and propellant samples have shown no detrimental aging effects due to the presence of the cure catalyst. The CrOct catalyzed propellants age as well as 140°F cured control propellants.

5. The Telagen-epoxide ambient-cured binder system is ready for scale-up beyond the 40-lb. batch scale size, 85.5% total solids propellant demonstrated in this program.

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Carboxy Terminated Binders						
Cure Catalysts						
Ambient Temperature Cure						
Epoxy Curatives						
Organometallics						
Solid Propellants						
Aziridine Curatives						
Organometallic Cure Catalysts						
Telagen CT						
PBAN						
HC 434						